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THE SIGNIFICANCE AND CONTROL OF WASTE-
WATER FLOATABLES IN COASTAL WATERS

Robert E. Selleck, et al

California University

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Abstract Significance of flotage derived from submerged primary effluent plumes in the Southern California Bight is evaluated in terms of three components: particulates > 0.5 mm in size, particulates ≤ 0.1 mm in size, and surface film materials. The sampling methods utilized to collect the flotage from the surface are described in detail. The surface film and micro-particulates were captured by fabric screen samplers developed during the course of the study.

It was found that the large particulates penetrated the ocean thermocline and gathered on the surface in profusion. The grease and wax portions of the particulates could be measured reliably with hexane extraction, with the mass of HEM of sewage origin being in the order of a metric ton on the water surface within the study area. Such particulates contained considerable numbers of coliform bacteria but little PCB compounds or pesticides.

The surface film materials and/or micro-particulates contained significant concentrations of coliform organisms and PCB compounds, but not pesticides. The HEM derived from this type of flotage may have amounted to 300 kg on the water surface within the study area in July 1973. Regulations for controlling the concentration of flotage on the ocean surface are suggested after considerable discussion.

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THE SIGNIFICANCE AND CONTROL OF WASTEWATER
FLOATABLES IN COASTAL WATERS

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ABSTRACT

The significance of flotage derived from submerged primary effluent plumes in the Southern California Bight is evaluated in terms of three components: particulates ≥ 0.5 mm in size, particulates ≤ 0.1 mm in size, and surface film materials. The sampling methods utilized to collect the flotage from the surface are described in detail. The surface film and micro-particulates were captured by fabric screen samplers developed during the course of the study.

It was found that the large particulates penetrated the ocean thermocline and gathered on the surface in profusion. The grease and wax portions of the particulates could be measured reliably with hexane extraction, with the mass of HEM of sewage origin being in the order of a metric ton on the water surface within the study area. Such particulates contained considerable numbers of coliform bacteria but little PCB compounds or pesticides.

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Regulations for controlling the concentration of flotage on the ocean surface are suggested after considerable discussion.

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I. CONCLUSIONS

The following applies to primary (or a combination of primary and secondary) wastewater effluent plumes submerged 12 to 30 m beneath the ocean surface.

TRAWLED PARTICULATES (≥ 0.5 mm in size)

1. Grease and wax particulates always predominated over all other sewage types. The mean grease and wax particulate found over the marine outfalls had the following characteristics:

Size = 1.3 mm

Hexane Extractable Materials (HEM) = 1.0 mg

Coliform Bacteria $\sim 2 \times 10^4$ organisms

Composition of HEM

PCB < 0.10%

Free Fatty Acids = 10%

Fats = 20%

Alkanes = 20%

Unidentified Long-Chain Organics = 10%

Bound Water = 40%

Their size remained constant regardless of distance from the outfalls but their free fatty acid composition altered significantly.

2. The number of grease and wax particulates found in a sample usually correlated directly with the mg of HEM extracted from the sample, regardless of location. Interferences in the correlation were caused by pieces of tar.

3. The mass of HEM on the water surface within the study area may have averaged approximately 840 kg during the surveys of 1971 and 1973. The concentration of HEM ranged from a maximum of approximately 33 mg/m² over the outfalls to a minimum of 0.001 mg/m² in the control areas.

4. The free fatty acid compositions of particulates strained from the JWPCP effluent and collected over the outfalls at the same time were nearly identical.

5. Local mass balances made about the marine outfalls indicated that an appreciable portion of the large particulates must have attained the ocean surface even when the effluent plumes were submerged.

6. Evidence indicates that the grease and wax particulates can persist for long periods of time in the marine environment. Their ultimate destination was not ascertained definitively but a study using floating polyethelene pellets indicated that the particulates could move with the band type of sea slicks. The band slicks formed under wind speeds of less than 3-4 m/s. They always moved toward the mainland, independent of the wind direction and probably were associated with the internal waves, moving with the same speed and in the same direction as the internal waves. When the wind speed exceeded 4 m/s the band slicks were destroyed quickly and Langmuir mixing cells formed. The particulates were then either transported downwind or submerged under the ocean surface.

7. The mass emission rate of particulate HEM from the Hyperion and JWPCP outfalls was estimated to be approximately 1000 kg/day. In light of No. 3 above this implies a surface residence time of only one day in the study area. Either the particulates clustered in regions not sampled, or they were moved quickly out of the study area by wind and band slick influences of the type described in No. 6 above.

8. The grease and wax particulates contained from 2×10^3 to 2×10^4 coliform bacteria per mg of HEM within the vicinity of the marine outfalls. The bacteria were found in particulates captured as far as 4 km from the Hyperion outfall.

9. A suggested surface pollution control requirement for HEM, based on aesthetic and coliform bacteria considerations, is 1.0 mg/m² or less (exclusive of tar). This is 10 times lower than the current State of California requirement for ocean waters. No control requirement for nonextractable particulates is suggested because their concentrations were too small to be aesthetically objectionable, and their ecological significance was unknown to these investigators.

MICRO-PARTICULATES (<0.1 mm in size)

1. The surface concentration of the micro-particulates exceeded a million/m² at times. Their overall volume per unit surface area may have been greater than the trawled particulates and their sizes ranged from the minimum detectable limit of approximately one μ to 100 μ .

2. The concentrations and types of micro-particulates observed varied grossly between the two surveys of 1971. Their overall concentration generally was 2 to 3 times greater over the Hyperion outfall than elsewhere but their sources or chemical composition were not ascertained. Sampling for micro-particulates was discontinued after 1971.

SURFACE SCREEN SAMPLES

1. The glass cloth sampler collected duplex and stable monolayer surface films accurately (within approximately 10% for duplex films and 5% for monolayers).

2. PCB compounds appeared to be concentrated in the sea slicks found over the marine outfalls. A volumetric concentration as high as 0.8 mg/l as Aroclor 1254 was found over the Hyperion outfall in April 1971.

3. The average surface concentration of PCB was estimated to be 2.8 $\mu\text{g}/\text{m}^2$ (or 19 $\mu\text{g}/\text{l}$) as Aroclor 1254 in the study area in July 1973. The bulk ocean water concentration 0.5 m below the surface averaged about 0.050 $\mu\text{g}/\text{l}$. These data indicate that the PCB compounds were concentrated by a factor of at least 380 times on the ocean surface.

4. The surface and bulk water concentrations of PCB were four times higher in the region of the JWPCP outfalls than in the control area in July 1973, or twice the average values found throughout the study area at that time. The wastewater mass emission of PCB to the study area may have ranged from 3 to 10 kg/day as Aroclor 1254, but the significance of this material in terms of ocean surface pollution could not be ascertained because the surface PCB compounds could have been derived from atmospheric fallout as well as wastewater discharge. Concentrations of pesticides were always at least 10 times less than the PCB compounds in the 1973 survey.

5. Coliform bacteria were found in the screen samples collected over the wastewater outfalls in 1971. (No bacterial samples were collected in 1973.) The surface concentration very nearly exceeded 1000 organisms/ m^2

in 20% of the samples taken. This level corresponds to a volumetric concentration of at least 1000 organisms/100 ml. No coliform bacteria were found in 100 ml bulk water samples collected 10 cm underneath the ocean surface, nor in regions well removed from the marine outfalls.

6. The average surface concentration of free stearic acid (C_{18}) was estimated to be $4.0 \mu\text{g}/\text{m}^2$ (or $27 \mu\text{g}/\text{l}$) in the study area in July 1973. The concentration was 20 times higher over the JWPCP outfalls than in the control area, or more than three times the average study area value. The proportion of free stearic acid in the HEM decreased from 1.4% over the JWPCP outfalls to 0.33% in the control area. The bulk ocean water concentration of stearic acid (salts and free) 0.5 m below the surface was approximately constant at $1.0 \mu\text{g}/\text{l}$, regardless of location.

7. Very little free stearic acid was recovered from JWPCP effluent diluted with sea water in a pan in July 1973. The diluted effluent contained $150 \mu\text{g}/\text{l}$ of stearic acid for a total of 5.4 mg, but only 0.3% of this free stearic acid was recovered in six cloth samples taken consecutively from the water surface. The free stearic acid comprised on the average about 2.0% of the surface HEM.

8. In light of No. 6 and 7 above it was concluded that the free stearic acid was recovered primarily from micro-particulates which inhibited the salting out of this acid. This conclusion conforms to theory as well as such theory is known.

9. Using the free stearic acid as a tracer of micro-particulates of wastewater origin, the surface HEM derived from wastewater emissions was estimated to be 300 kg in the study area in July 1973.

10. The HEM determinations proved of little value in ascertaining surface pollution of wastewater origin, or the reason for the existence of sea slicks. The observed concentrations were highly variable, ranging from 0.9 to $3.9 \text{ mg}/\text{m}^2$ over the marine outfalls and from 0.16 to $2.0 \text{ mg}/\text{m}^2$ in the control areas.

11. The HEM analysis can be used only to control surface pollution resulting from duplex (oil) films or unusually high concentrations of wastewater micro-particulates. It is too gross a measure to control any pollution existing in the form of surface monolayers.

12. At the present time only the coliform bacteria analysis can be used to reliably control surface pollution derived solely from wastewater discharges. A criterion of 1000 total coliform organisms per m^2 of ocean surface is suggested but with reservation because such a criterion could prove to be extremely difficult to meet.

II. RECOMMENDATIONS

1. A great amount of work remains to ascertain the composition and mode of formation of sea slicks. Much of this would be strictly of scientific interest, but it would provide a better means of estimating the proportion of the surface film material derived from wastewater discharges as well as its ultimate destination. For example, reliable methods of acidifying and saponifying the glass cloth samplers should be developed to increase the yield of HEM and fatty acids. Also, the relationship between the fatty acids and their salts at the ocean interface has to be more fully understood with the aid of laboratory studies.
2. Reliable methods of sampling wastewater effluents for surface film forming substances remain to be developed. Simply screening from the top of effluent diluted with salt or fresh water yields information on the composition of the flotage, but not its total amount because an equilibrium appears to be established between the surface and bulk phase which is quickly reestablished upon removal of material from the surface. This process appears to continue indefinitely. It should be pointed out here that the composition of the flotage may differ appreciably between salt and fresh diluting waters.
3. The characteristics of the flotage, if any, derived from secondary effluents remains to be ascertained. It is possible that surfacing secondary effluent plumes could produce measurable quantities of surface flotage.
4. The effect of wastewater effluent chlorination on coliform bacteria contained in trawled and micro-particulates remains to be ascertained.
5. To complete the study discussed herein, measurements should be made on surfacing primary effluent plumes. This would enable a more direct means of establishing relationships between cause and effect. For example, the quantities of surface PCB compounds derived from a wastewater effluent could be determined quantitatively under such circumstances.

III. INTRODUCTION

The general objective of the first year of this study was to develop sampling and analytical techniques suitable for the evaluation of flotage at the surface of marine waters. Only a minimum of ocean work was to be carried out, primarily to determine the feasibility of the techniques developed and to obtain data for an initial assessment of the surface pollution problem. Emphasis was placed on the following items:

1. The development and evaluation of sampling and analytical techniques for surface films.
2. The development and evaluation of sampling and analytical techniques for floating particulates.
3. The development and evaluation of sampling and analytical techniques for other components of the flotage.
4. Evaluation of ocean data obtained in order to provide an initial assessment of the surface pollution problem.

The second year of the study was to be devoted primarily to ocean studies, the specific objectives of which were:

1. The measurement of flotage found in the vicinity of a marine outfall and comparison with that from a region free of water surface pollution.
2. Investigation of the mechanisms responsible for the concentration and movement of flotage on the sea surface during the periods of sampling.

The study objectives were also to include suggestions for the establishment of water surface quality requirements to be used for control of ocean surface and beach pollution.

The terms of the award made by the Environmental Protection Agency to The Regents of the University of California included the following conditions:

1. Both screen and trawled particulates will be characterized.

2. Particulates will be classified according to size.
3. The analysis of inorganic and organic parameters will be conducted on both film and particulates.
4. Coliform and, if possible, virus concentrations of film and particulates will be enumerated.
5. The wastes sampled in the ocean will be correlated with raw water samples, preferably by sampling from the same waste volume.

The only one of those conditions which modified substantially the proposed work was item 4, i.e., "Coliform and, if possible, virus concentrations of film and particulates will be enumerated." After consultation with the Project Officer, it was agreed that virus enumerations could not be carried out without considerable cost and therefore would not be included. Coliform organism determinations were initiated immediately, however.

Subsequent to the awarding of this grant, the Southern California Coastal Water Research Project (SCCWRP) requested that the sampling and analytical techniques developed in the first year of this study be used in fairly extensive ocean studies of surface conditions in the Southern California Bight. This was well removed in distance from the sites envisaged originally for the ocean studies and the costs were increased appreciably. SCCWRP offered compensation in terms of furnishing the sampling craft and supporting the personnel needed for the ocean studies. Three separate ocean surveys were made in 1971 under this arrangement with the pertinent data being presented and discussed in this report. The ocean work of 1973 was conducted without any aid from SCCWRP but the studies were continued in the Southern California Bight area to complement the results of the 1971 work.

The participation of SCCWRP made it possible to collect data in a region of real concern to the public. Even so, the Southern California Bight region was not ideal for the development of new sampling and analytical tools because the large primary effluents were always submerged beneath the ocean thermocline during the ocean surveys and the region was remote from the sample processing laboratory. A more orderly procedure would have been the sampling of surfacing primary and secondary effluents first

to establish firmly cause and effect relationships.

Section IV of this report describes the character of the area sampled in the ocean surveys as well as the conditions encountered during each survey. General information on the techniques employed in each survey is also presented in that section. Sections V, VI, and VII deal almost exclusively with the three types of sampling techniques evaluated during the study: surface trawling, nylon netting screens, and glass cloth screens. Wastewater effluent sampling of concern to each of those techniques is presented at the appropriate time.

IV. DESCRIPTION OF OCEAN SURVEYS

This study was conducted in the San Pedro Channel and Santa Monica Bay regions of the Southern California Bight as shown in Figure 1. Sampling Stations 1 and 4 were located over the marine outfalls of the Hyperion Plant of the City of Los Angeles and the Joint Water Pollution Control Plants (JWPCP) of the County of Los Angeles, respectively. Station 2 was located 3.7 km north of the Hyperion outfall and Station 5 west of the Palos Verdes Peninsula at the latitude of the Marineland of the Pacific. This station will be called "Marineland" at times in this report and it was located approximately 14 km northwest along the coast from the JWPCP outfalls.

Stations 3a and 3b were selected as control areas. They were located at the northern end of Santa Catalina Island and out of the main surface circulation pattern of Santa Monica Bay. This region was approximately 44 km south of the Hyperion outfall and 33 km southwest of the JWPCP outfalls.

Three field surveys were conducted in 1971. The objectives of the first two, performed on April 7-8 and August 31-September 3, were to evaluate various means of sampling the water surface for flotage, the identification of surface pollution, and the significance of sea slicks in concentrating the flotage. The third survey of December 9 was for the purpose of tracing the movement of flotage on the sea surface.

The data procured from the 1971 surveys were analyzed and a fourth survey of the study area was made on July 11-13, 1973. The major emphasis of that survey was placed on surface film sampling because the results of the 1971 surveys were inadequate in some respects for this type of sampling.

The two outfall systems sampled, JWPCP and Hyperion, had about equivalent flows and contributed together about 71 percent of the total wastewater flow released to the California Bight in 1971 [1]. The two other major dischargers, Orange County and San Diego, were located many kilometers south of the study area. The dimensions of the outfalls sampled are presented

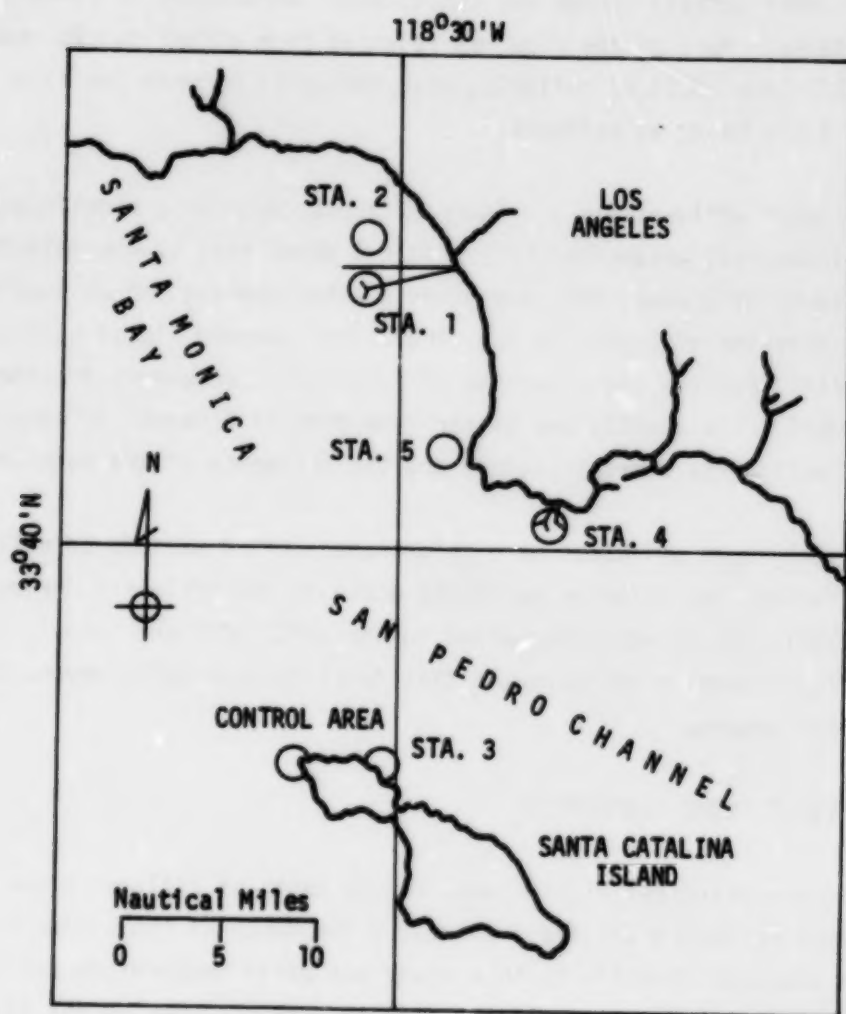


Figure 1. Study Area

in Table 1 together with the average 1971 flows and effluent quality characteristics.

The JWPCP outfall system was complicated, consisting of three separate outfalls. Most of the flow was released from either the 90 inch (2.29 m) or 120 inch (3.05 m) outfalls, with the split between the flows shown in the table being an estimate.

The JWPCP effluent was a primary effluent containing significant portions of industrial wastewater [1]. Table 1 shows that it was relatively strong in terms of grease, BOD, and other routine measures of wastewater quality. The Hyperion effluent, on the other hand, stemmed almost entirely from domestic sources and a portion of it received secondary treatment (activated sludge). Its quality was better than that of a normal primary effluent, reflecting its domestic nature and the influence of the secondary treatment.

Commonly both effluents were chlorinated during periods of effluent plume surfacing. No chlorine was being added to the effluents during the surveys of 1971, but it was being added to the JWPCP effluent in July 1973. All effluent samples collected at that facility were taken beyond the chlorination process.

EFFLUENT PLUME SUBMERGENCE

Of great practical significance is the depth of effluent plume submergence occurring during the field surveys. The depth of the effluent plumes were not measured directly in this study but water temperature and salinity were measured with depth at all the stations occupied during the first two surveys. The results showed that most of the density structure resulted from temperature variation and only the observed temperature and computed density profiles are shown in Figures 2, 3, 4, and 5. Water temperatures only were measured during the July 1973 survey with the results being presented in Figure 6.

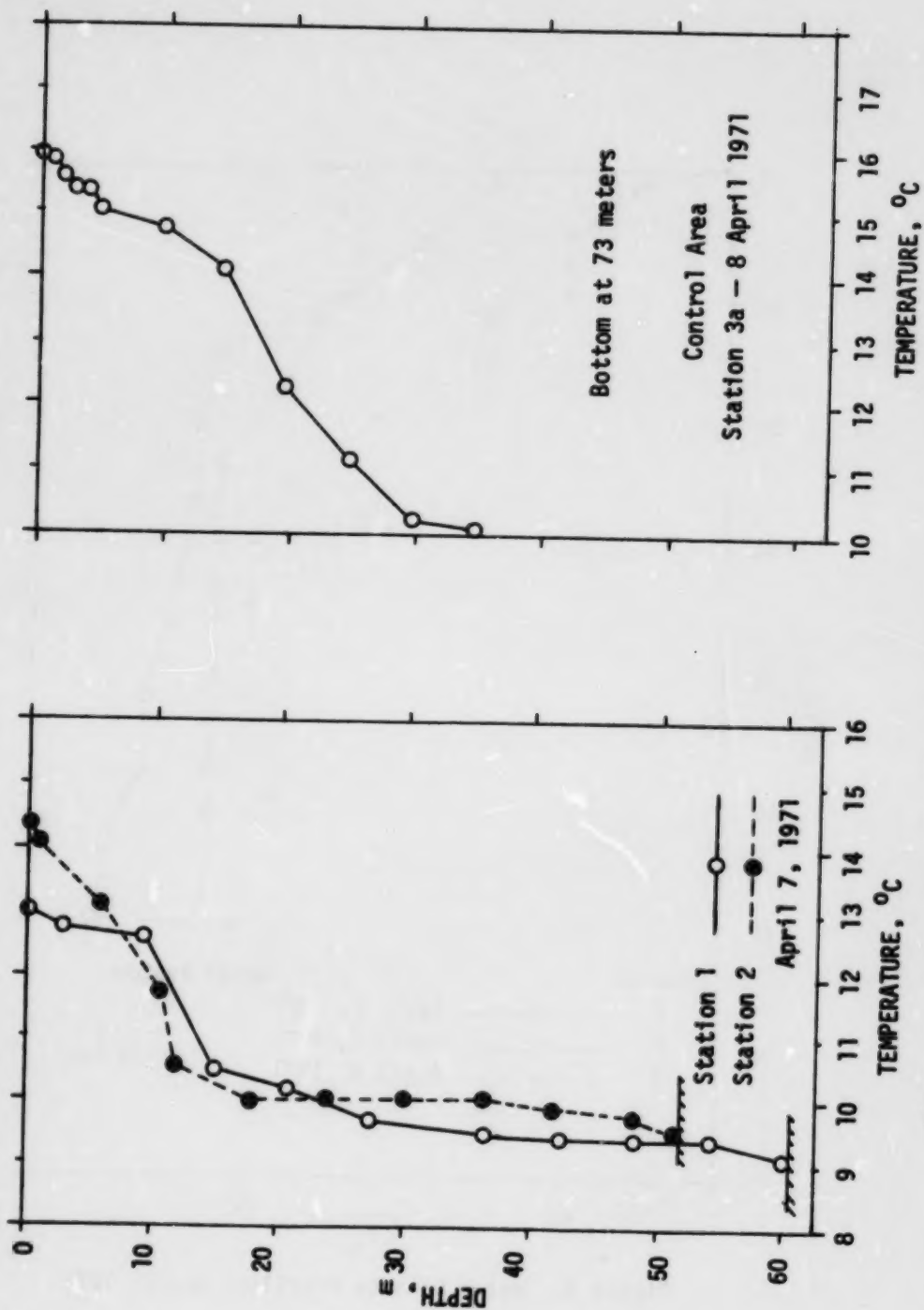


Figure 2. Temperature Profiles Observed at Sampling Stations: April, 1971

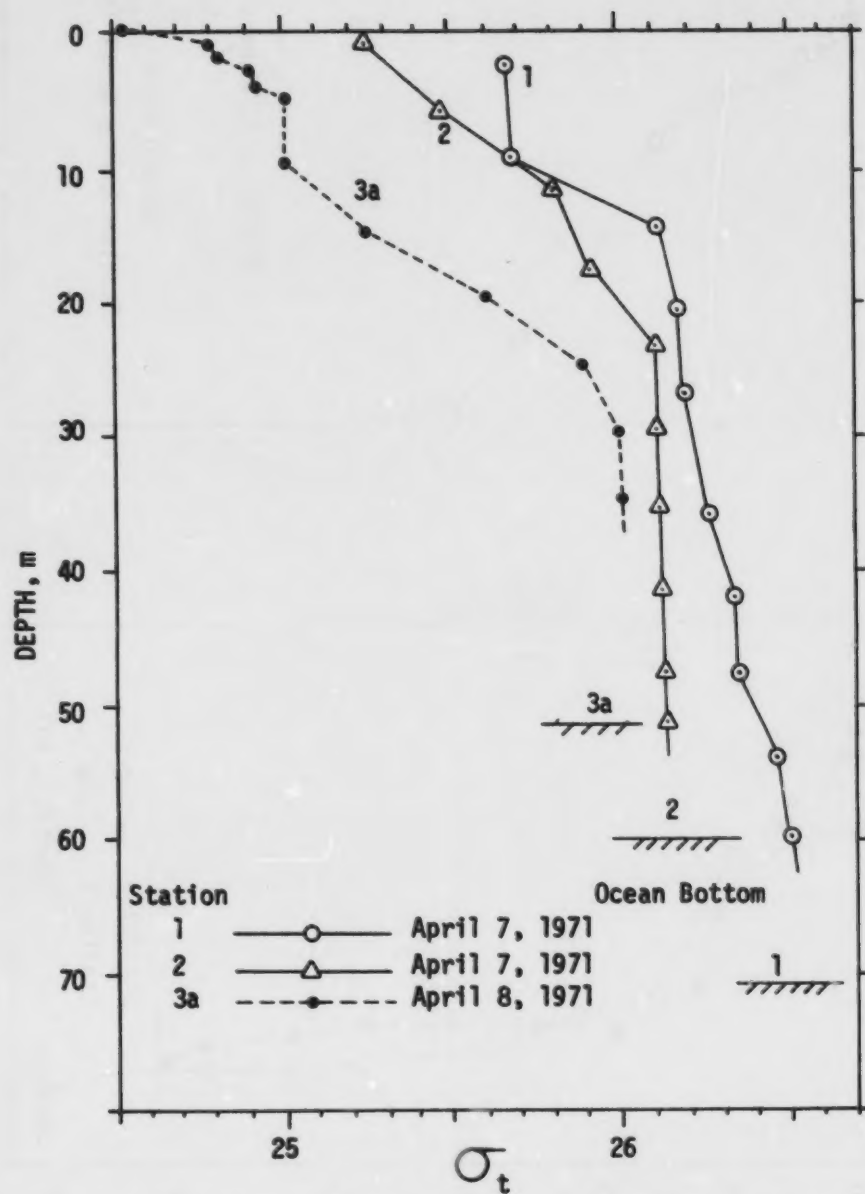


Figure 3. Water Density Profiles: April, 1971

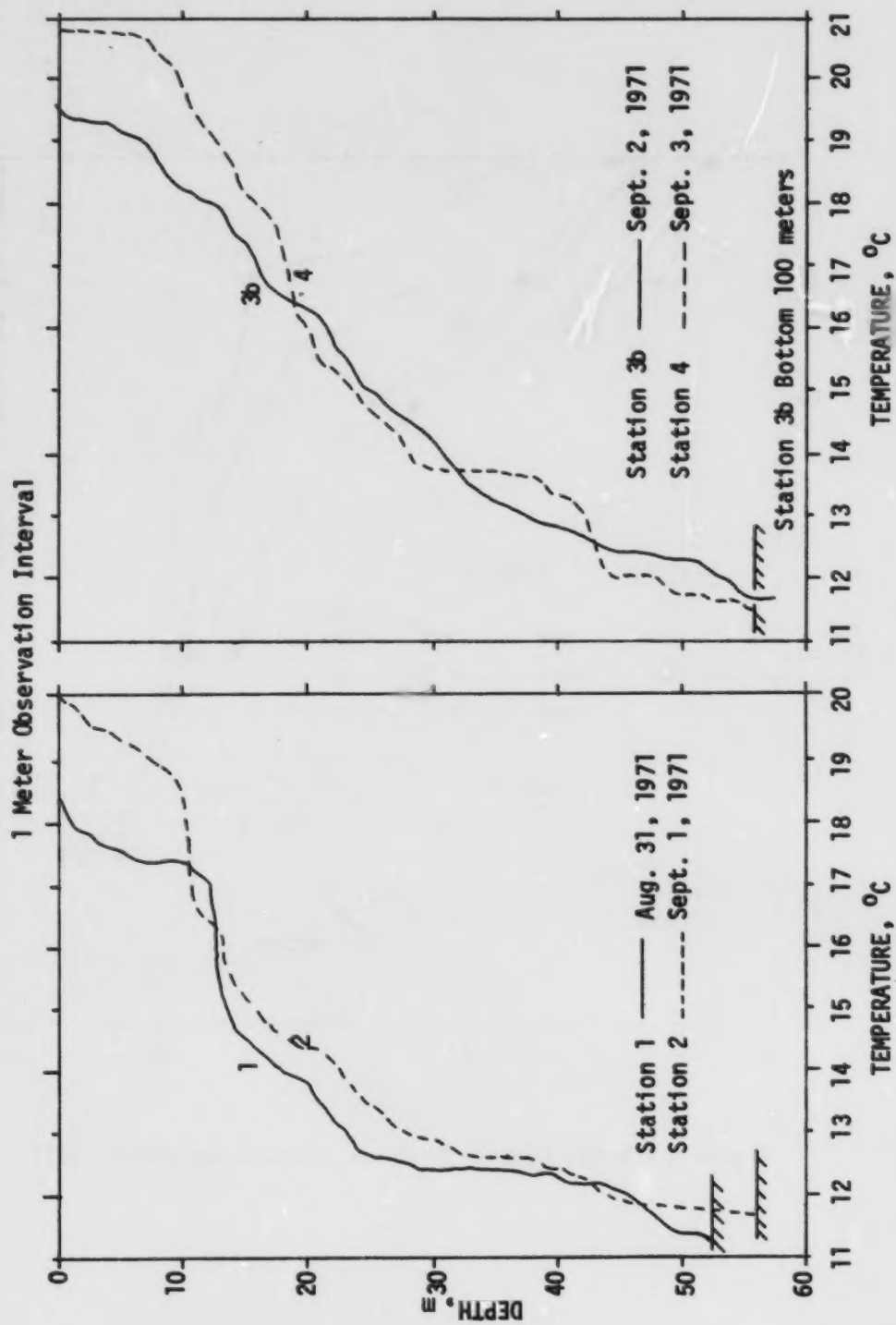


Figure 4. Temperature Profiles Observed at Sampling Stations: August-September, 1971

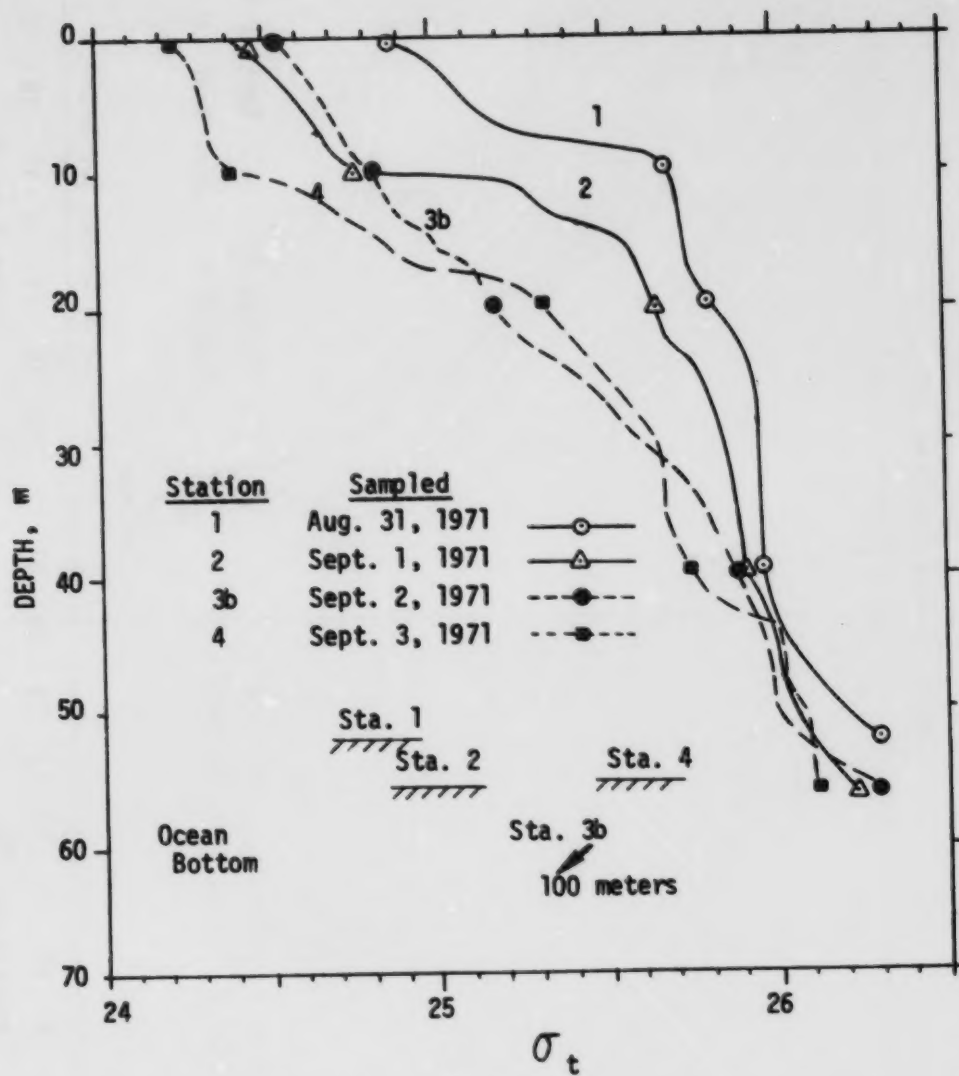


Figure 5. Water Density Profiles: August-September, 1971

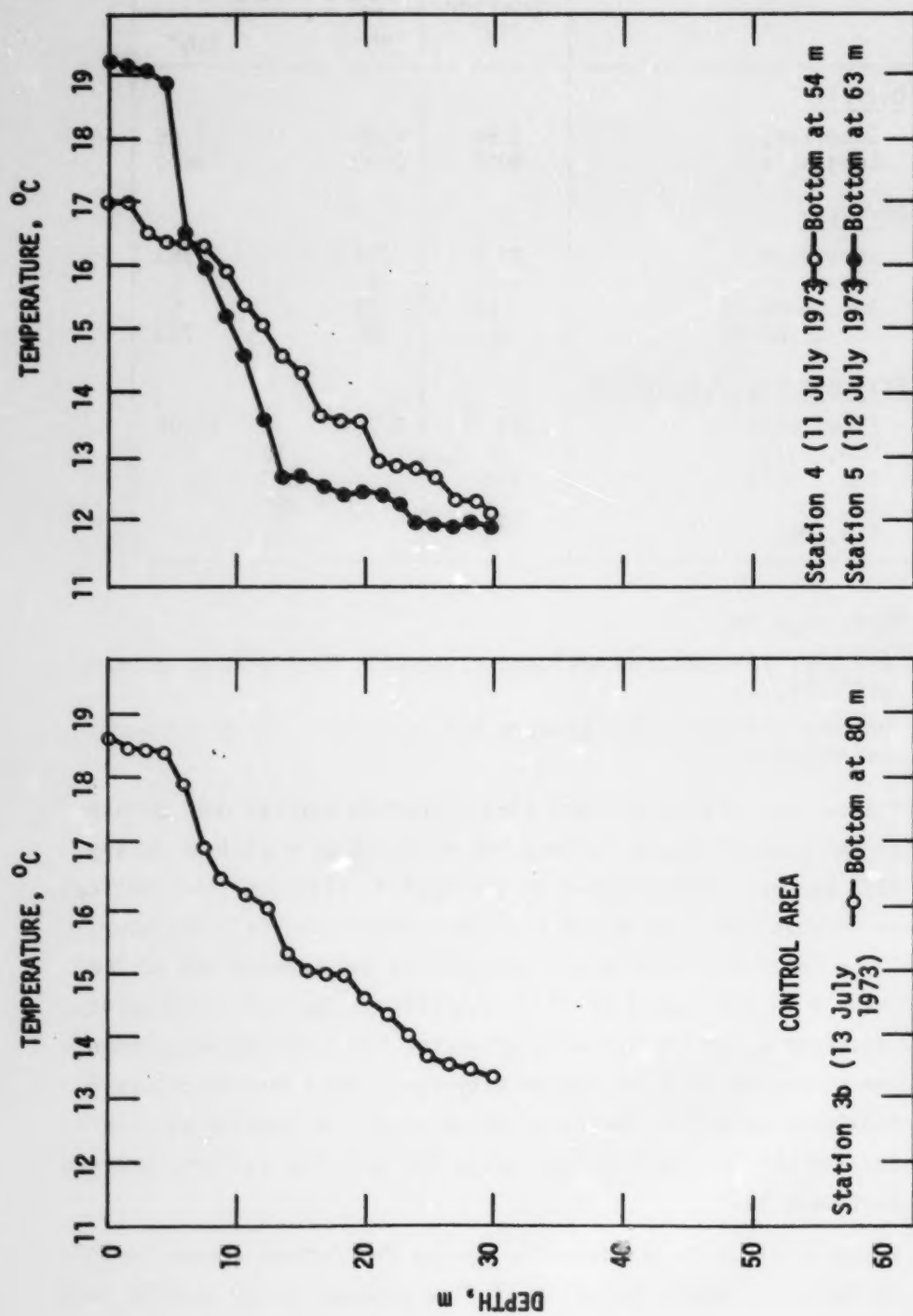


Figure 6. Temperature Profiles Observed at Sampling Stations: July 1973

Table 1. CHARACTERISTICS OF OUTFALLS SAMPLED

	Hyperion 144"	JWPCP outfalls	
		90"	120"
<u>Outfall</u>			
Diameter, m	3.66	2.29	3.05
Length, m	8000	2600	3600
<u>Diffuser</u>			
Length, m	2414	732	1353
Shape	Y	Y	L
Av. depth, m	59	63	56
No. of ports	168	100	740
<u>Effluent (av. for 1971)^a</u>			
Flow, m ³ /s	14.7 ^b	5.26 ^c	11.0 ^c
HEM, mg/l	19		70
BOD ₅ , mg/l	120		320
SS, mg/l	73		330
VSS, mg/l	55		210

^aData from Ref.

^b4.4 m³/s of secondary effluent mixed with 10.3 m³/s of primary effluent.

^cPrimary effluent split between two outfalls, Flows in each estimated.

The figures show that extensive ocean stratification existed during those surveys with the overall change in temperature being at a minimum during the April 1971 survey. With respect to the outfall stations, the vertical profiles were always measured in the Y of the Hyperion outfall diffuser. At the JWPCP outfalls the profile was measured at the seaward end of the L shaped diffuser in the summer of 1971, and also in the July 1973 survey. Only a few discrete water samples were collected for salinity measurements in the summer survey of 1971, so the density structure shown in Figure 5 is only approximate except at the data points shown. A density structure was estimated for the July 1973 survey using the salinity pattern observed in August-September 1971.

The daily flows existing in the outfalls during the various survey periods are shown in Table 2. Again the split of flow between the 90 and 120 inch

Table 2 . CALCULATED PLUME SUBMERGENCE AND DILUTION
OVER MARINE OUTFALLS

Outfall	Date	Daily flow m ³ /s	Plume submergence m	Initial dilution
Hyperion	IV-7-71 VIII-31-71	14.9 15.2	12 21	100 90
JWPCP				
90"	IX-3-71 VII-11-73	5.4 5.1	33 17	100 (a)
120"	IX-3-71 VII-11-73	11.3 10.6	33 15	70 (a)

^aNo submarine currents measured.

outfalls of the JWPCP facility was estimated. Using these data plus the density gradients measured or estimated at each outfall, the rise of the effluent plumes above the diffusers was estimated using the methods of Brooks [2]. In the case of the two older Y shaped diffusers it appeared that the jets derived from the rather widely spaced ports would rise more or less independently without much overlap, but the jets from the L shaped diffuser would soon overlap giving continuous curtains of rise. The results of these computations in terms of plume submergence are presented in Table 2.

Initial dilutions over the outfalls were also estimated using the methods of Brooks [2] as well as the continuity equation in those cases where the currents had been measured with depth. In general the continuity approach yielded the lesser initial dilution values and those estimates are presented in Table 2 along with the estimates of plume submergence. The current data utilized for this purpose are tabulated in Tables 1 and 2 of Appendix A.

The results shown in Table 2 indicate a minimum plume submergence over the Hyperion outfall on April 7, 1971; being at a depth of only 12 m or so. Maximum submergences of 20 m or greater may have occurred in the summer survey of 1971. The plume submergences computed for the July 1973 survey

appeared to be less than those obtained for the summer 1971 survey but the latter computations have to be considered as being very approximate.

In most cases the initial dilution may have been nearly 100-fold over the outfalls, checking with some of the observations of water quality made in the Southern California Coastal Water Research Program Study [1].

The significant finding of all this is that the wastewater effluent plumes were submerged beneath the pycnocline during the times when flotage was collected from the ocean surface. A minimum submergence of 12 m may have existed in the Hyperion area in April 1971. These computations check well with visual observations of the sea surface made during the ocean surveys as discussed below.

SURFACE CONDITIONS DURING SURVEYS

The success of a program of ocean surface sampling is dependent on the weather conditions encountered. By far the most significant influence is the wind. A strong wind will disrupt and disperse sea slicks quickly and eventually submerge even fairly large floating particulates. A light breeze is not detrimental in some respects but the sea slicks become invisible quickly either because the wind is insufficient to ripple areas not covered by a surface film, or because the film itself has an opportunity to form across the entire surface. Sea swell makes accurate surface sampling more difficult but it has little effect on the sea slicks. The effects of water density stratification and internal waves on sea slick visibility remains to be ascertained. Because the wind plays a significant role in surface sampling a detailed description of the wind conditions encountered during each survey is given below.

April, 1971

The best wind conditions were encountered in the very first survey of April 7-8, 1971. Numerous well-defined slicks were observed despite an appreciable sea swell. A 10 knot (5 m/s) wind did break up the slicks in the afternoon of April 7.

The most outstanding feature of the first survey was a large standing slick outlining the Hyperion diffuser on the morning of April 7 as shown in Figure 7. This slick was never observed subsequently. Other types of sea slicks were also observed in the area including a broad meandering slick directed more or less downcurrent from the diffuser and narrow band slicks running parallel to the coast at Station 2, 3.7 km north of the outfall diffuser. The slicks at Station 3a in the control area consisted of a large ill-defined slick lying in the lee of Santa Catalina Island and several band slicks as shown in Figure 8. The wind speed was ideal at 2-3 knots (1 to 1.5 m/s).

August-September, 1971

The wind was not particularly favorable for surface sampling during the summer cruise of 1971 and the sea slicks commonly were rather poorly defined. No wind existed in the Hyperion outfall region on the morning of August 31 and the slicks were nearly invisible. There was the hint of a series of band slicks moving across the diffuser in the shoreward direction, however, and these were sampled and called "slick samples." A strong southwest wind rose in the afternoon destroying any slick patterns which might have existed in the area.

Conditions were better in the early morning hours of September 1 and well-defined band slicks were observed 3.7 km north of the Hyperion outfall as shown in Figure 9. An east wind of 5 to 7 knots (2.5 to 3.5 m/s) existed at the time but this soon disappeared and the slicks became nearly invisible. At times the wind would gust briefly and a slick pattern would appear again. At noon the wind veered to the southwest and increased to 11 knots (5.7 m/s) and the surface was broken up entirely into downwind mixing cells.

The results of the first survey conducted in the control area on April 8, 1971 indicated that the surface may have been polluted slightly at Station 3a. The windward side of Santa Catalina Island was then selected as the

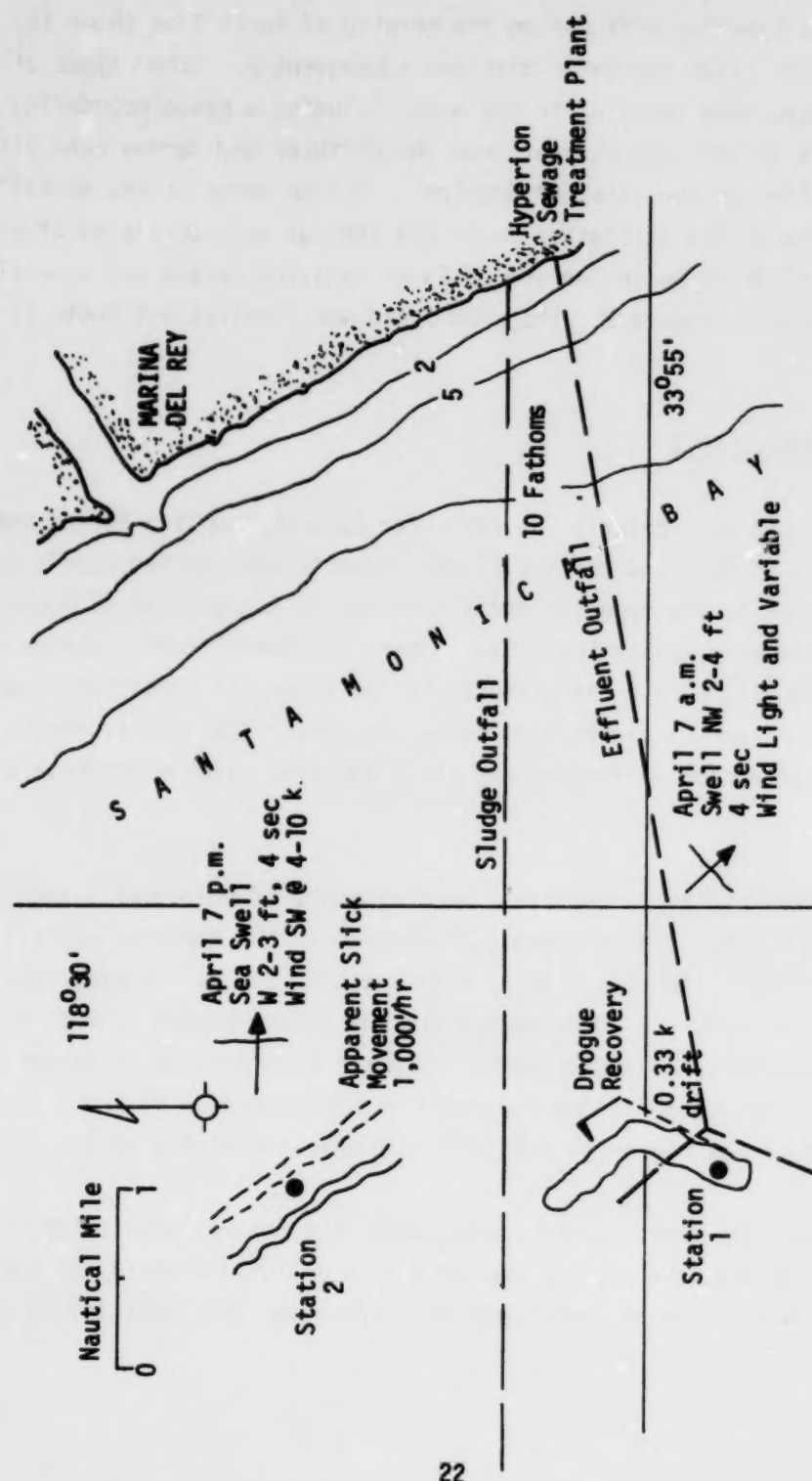


Figure 7. Surface Conditions in Hyperion Outfall Region: April 7, 1971

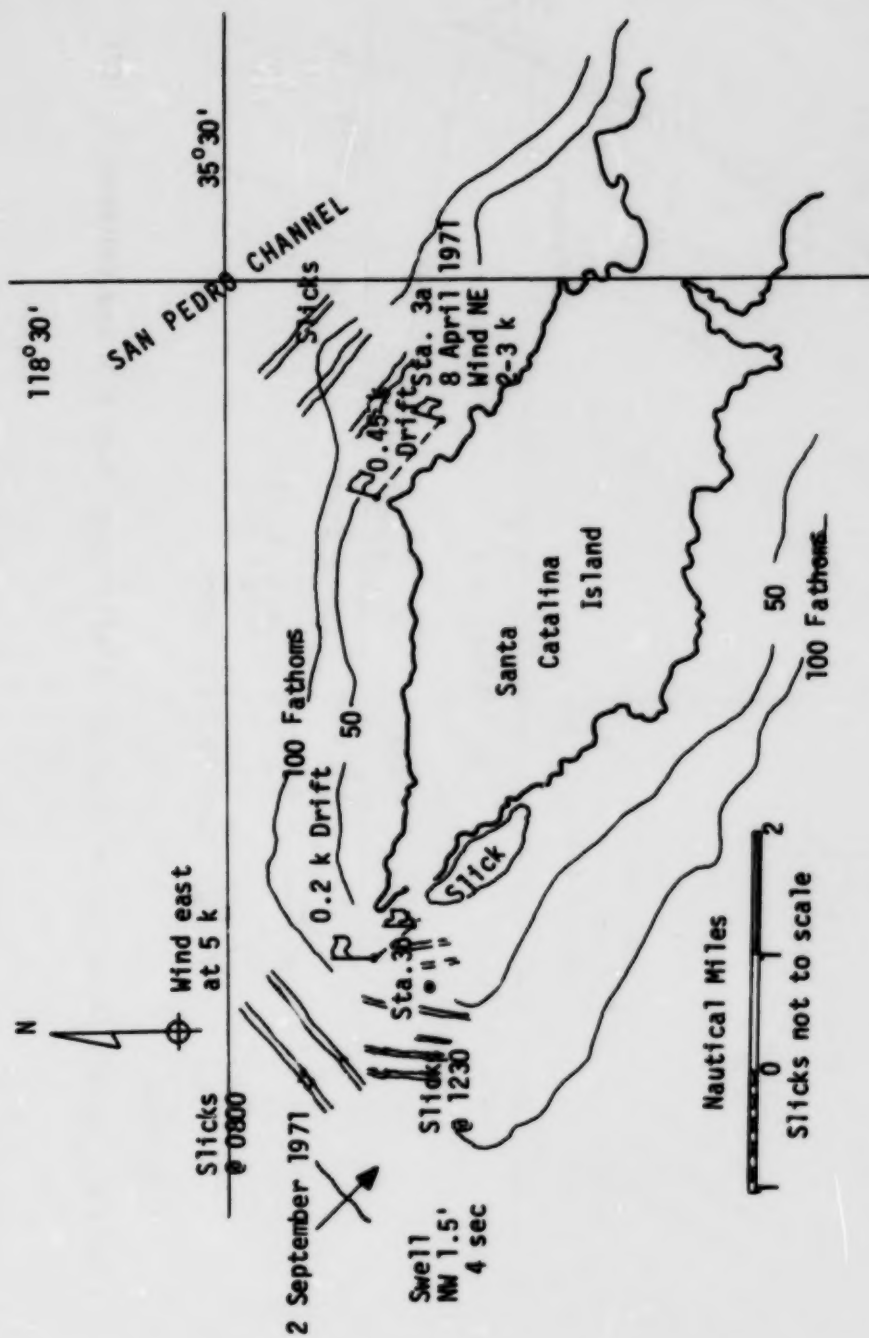


Figure 8. Surface Conditions in Control Areas: April 4 and September 2, 1971

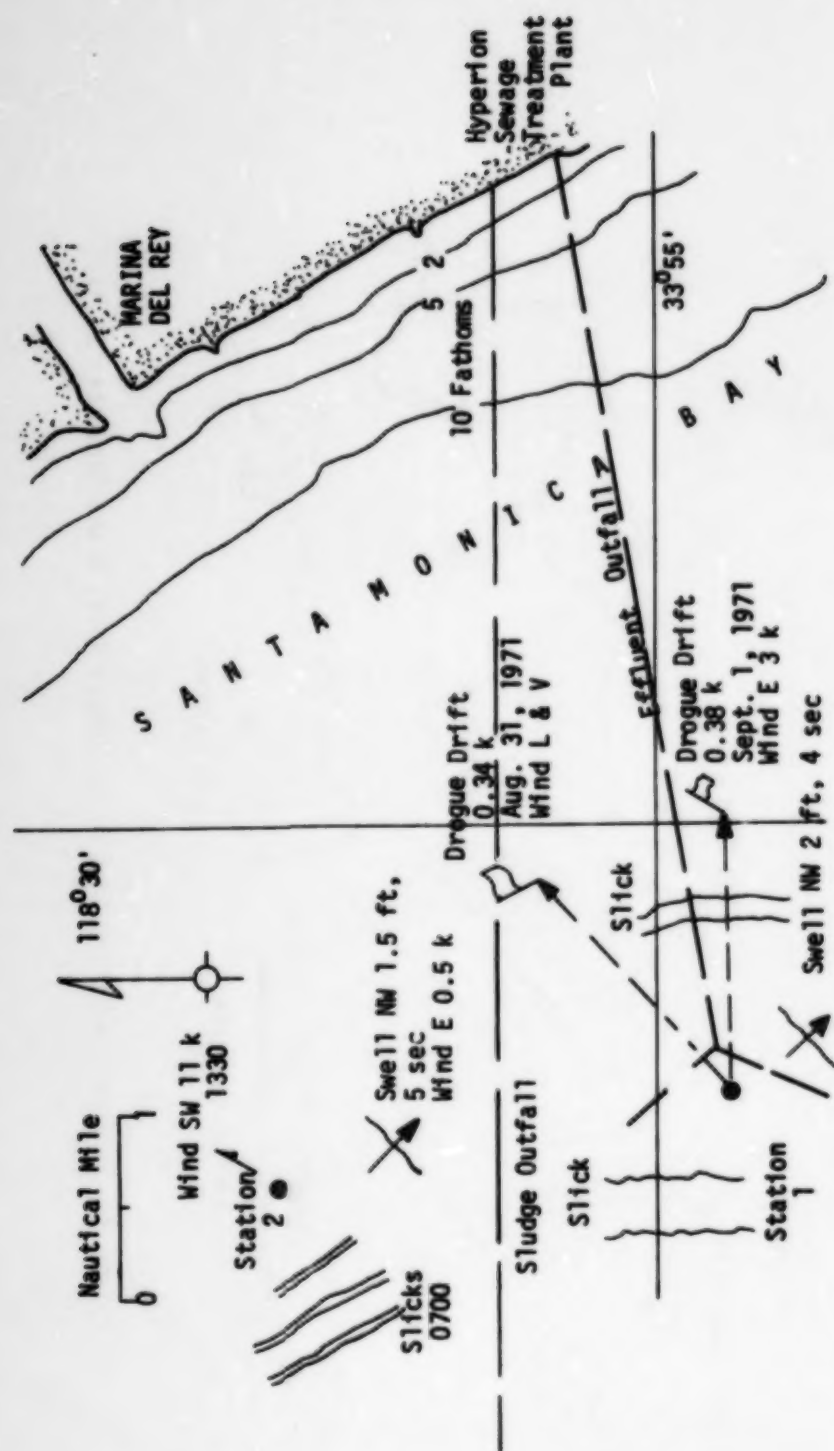


Figure 9. Surface Conditions in Hyperion Outfall Region: August 31 and September 1, 1971

control area and designated as Station 3b as shown in Figure 8. A steady 2.5 m/s east wind was favorable for sea slick visibility and a number of narrow well-defined slick bands were observed in the area.

The JWPCP outfalls were sampled on the morning of September 3, 1971 as shown in Figure 10. The wind averaged only about 7 knots (3.6 m/s) from the east during that time but no sea slicks were visible. The best that could be done was to allow the sampling craft to drift over the 90 inch Y diffuser while collecting film samples

December, 1971

A slick tracing study was conducted on December 9, 1971 as shown in Figure 11. A steady southwest wind in excess of 7 knots (3.6 m/s) persisted until mid-afternoon when it gradually decreased to a light air by sunset. No slicks were apparent anywhere along the coast until the wind began to decrease. A series of sharply-defined band slicks then appeared in the region where the sampling craft happened to be cruising at the time. Those slicks, shown in Figure 11, ran parallel to the coast and increased in width as the wind dropped until by sunset it appeared as if the entire surface was covered by a single slick.

July, 1973

Wind conditions were never very ideal during the July 1973 survey. The weather had been unsettled for weeks prior to the cruise, following a general pattern of strong winds in the afternoon and evening and mild winds in the early morning hours. The slicks themselves were always poorly defined and seemingly on the verge of disappearing.

The wind was calm over the JWPCP outfalls in the early morning hours of July 11, 1973 and no slick patterns were visible. Indeed, it appeared that the entire surface was one large slick. A 2 to 3 knot (1 to 1.5 m/s) west wind sprung up quickly after 8 a.m. and poorly defined patterns of broad, diffuse band slicks formed as shown in Figure 12. The majority ran normal

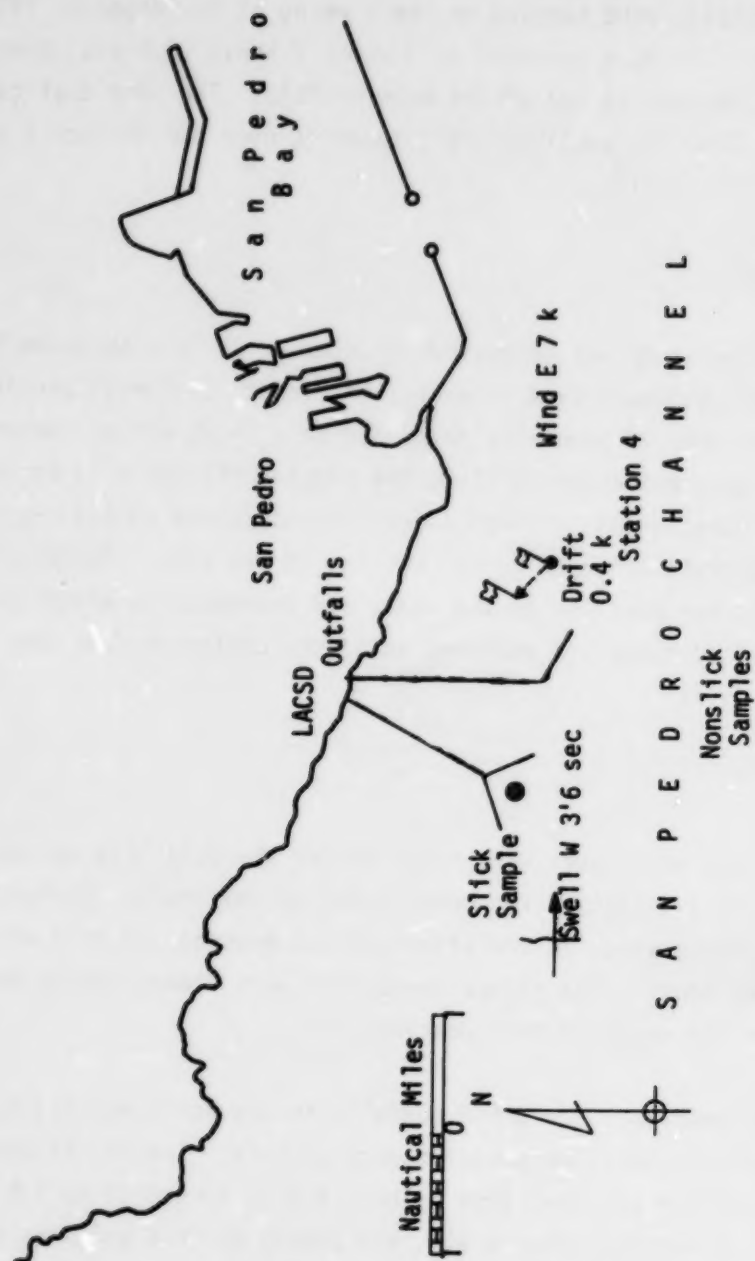


Figure 10. Surface Conditions Over JWPCP Outfalls: September 3, 1971

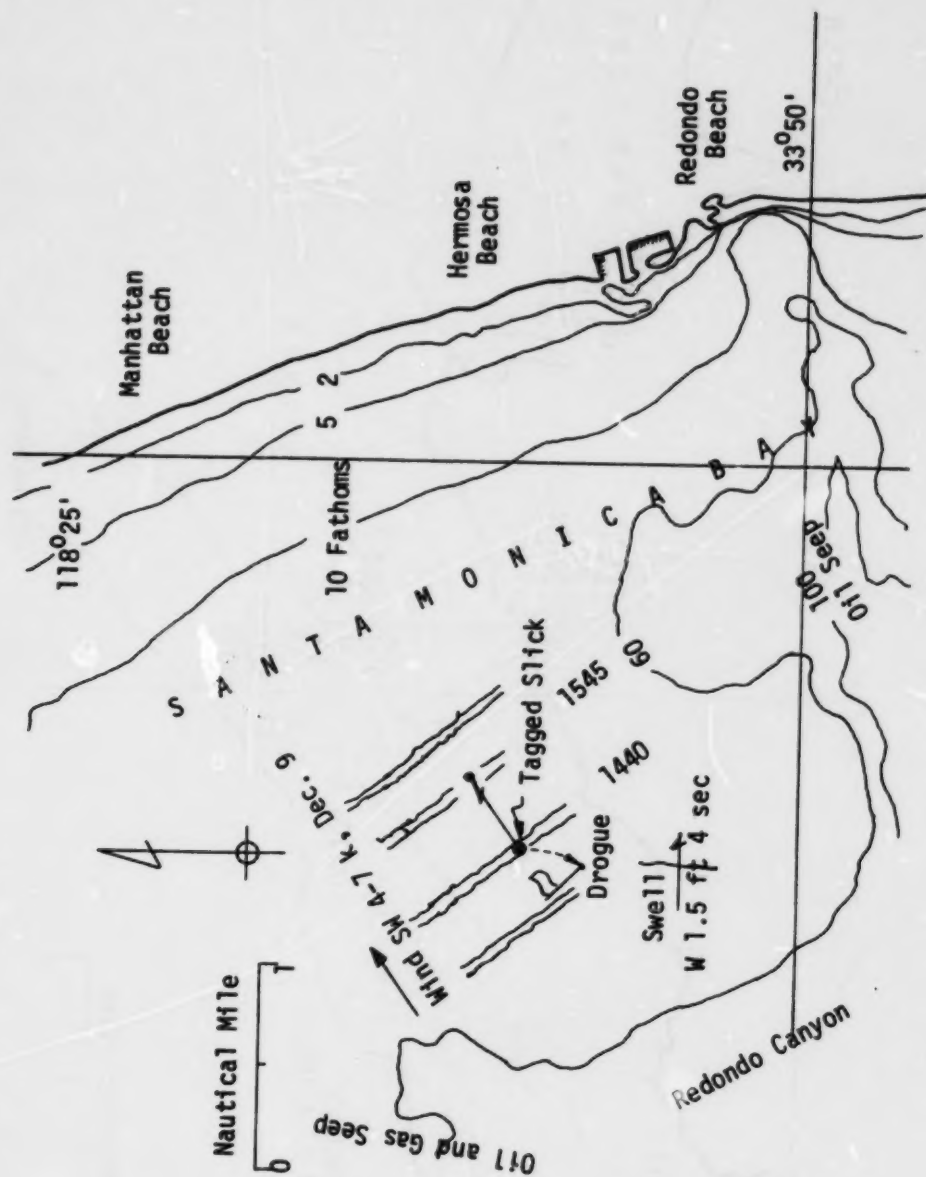


Figure 11. Transport of Flottage Study: December 9, 1971

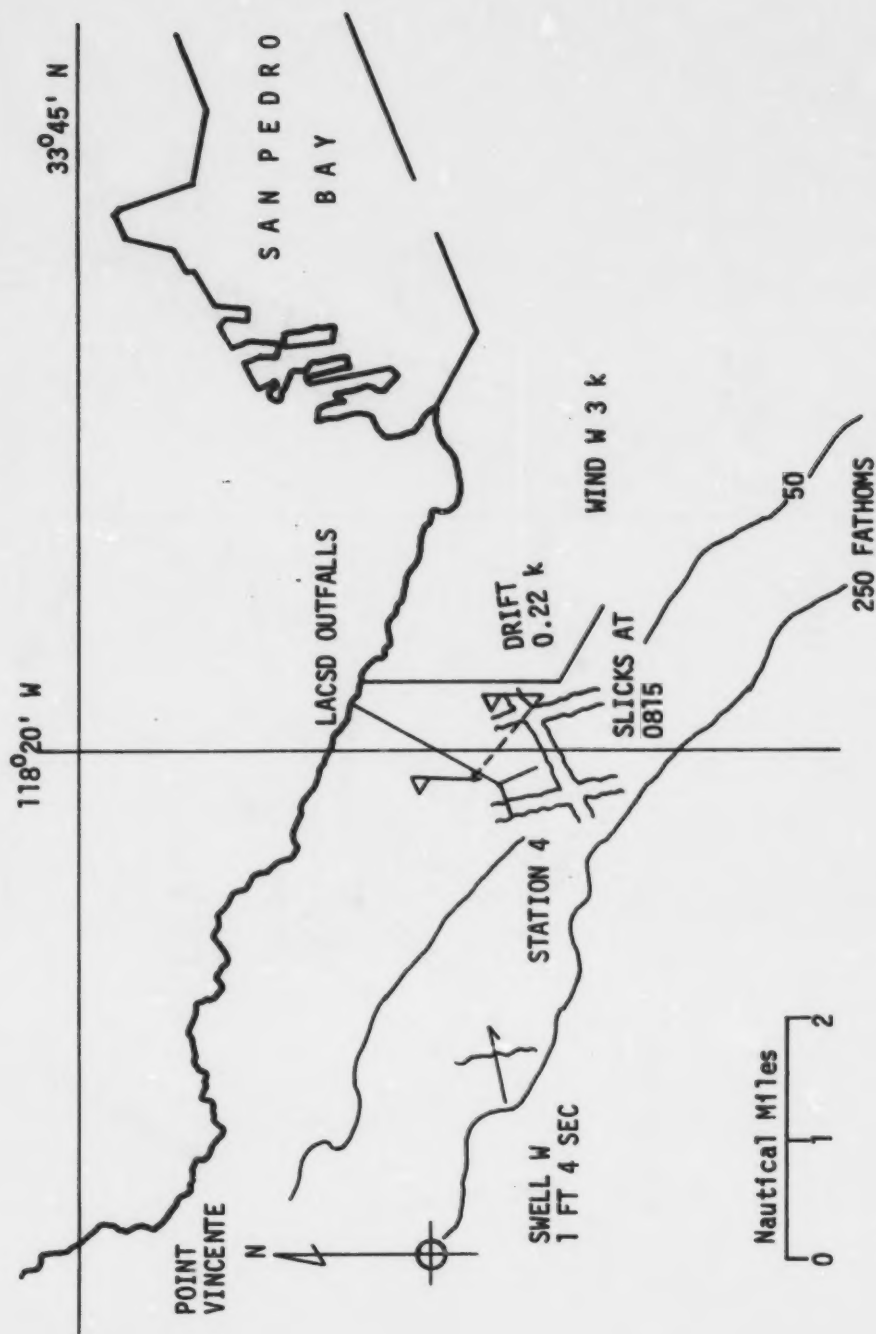


Figure 12. Surface Conditions Over JMWCP Outfalls: July 11, 1973

to the coast but some paralleled the coast, suggesting two independent slick patterns with one moving across the other. The wind increased to 7 knots (3.5 m/s) by noon and the slick patterns disappeared.

On the following day an easterly morning wind was much too strong to permit sea slick formation in the JWPCP outfalls area, but the land mass of the Palos Verdes Peninsula sheltered the waters lying to the west of the peninsula and a series of band slicks were found at the Marineland station shown in Figure 13. The wind in this region was from the east, approximately steady at 6 to 7 knots (3 to 3.5 m/s), and the slicks were broad and ill-defined, with some running normal and others parallel to the coast. By noon the slicks had been broken up and dispersed by the easterly wind.

A break in the wind pattern occurred on July 13, 1973 when unsteady westerly winds dropped from an average of about 6 knots (3 m/s) in the early morning hours to 4 knots (2 m/s) by noon. A series of band slicks were observed in the control area northwest of Santa Catalina Island (Station 3b) as shown in Figure 14. No interfering slick band patterns were observed and the slicks tended to run normal to the coast.

Photographs of the sea slicks observed in the summer 1971 and July 1973 surveys are shown in Figure 15 for the areas over the Hyperion and JWPCP outfalls. Unfortunately, photographs were not taken of the large standing slick found over the Hyperion outfall on April 7, 1971. (See page 117)

DISCUSSION

Very little information exists in the literature concerning the mode of formation or significance of wastewater sea slicks. One recent paper by Newton [3] describes the prevalence of sewage slicks in an estuary and some attempts were made to procure a mass balance on amounts of fats released and the extent of the resulting surface sewage films. Unfortunately, there exists orders of magnitude differences between that study and this, where the grease content of the effluents were grossly less and the effluent plumes remained submerged beneath the ocean thermocline.

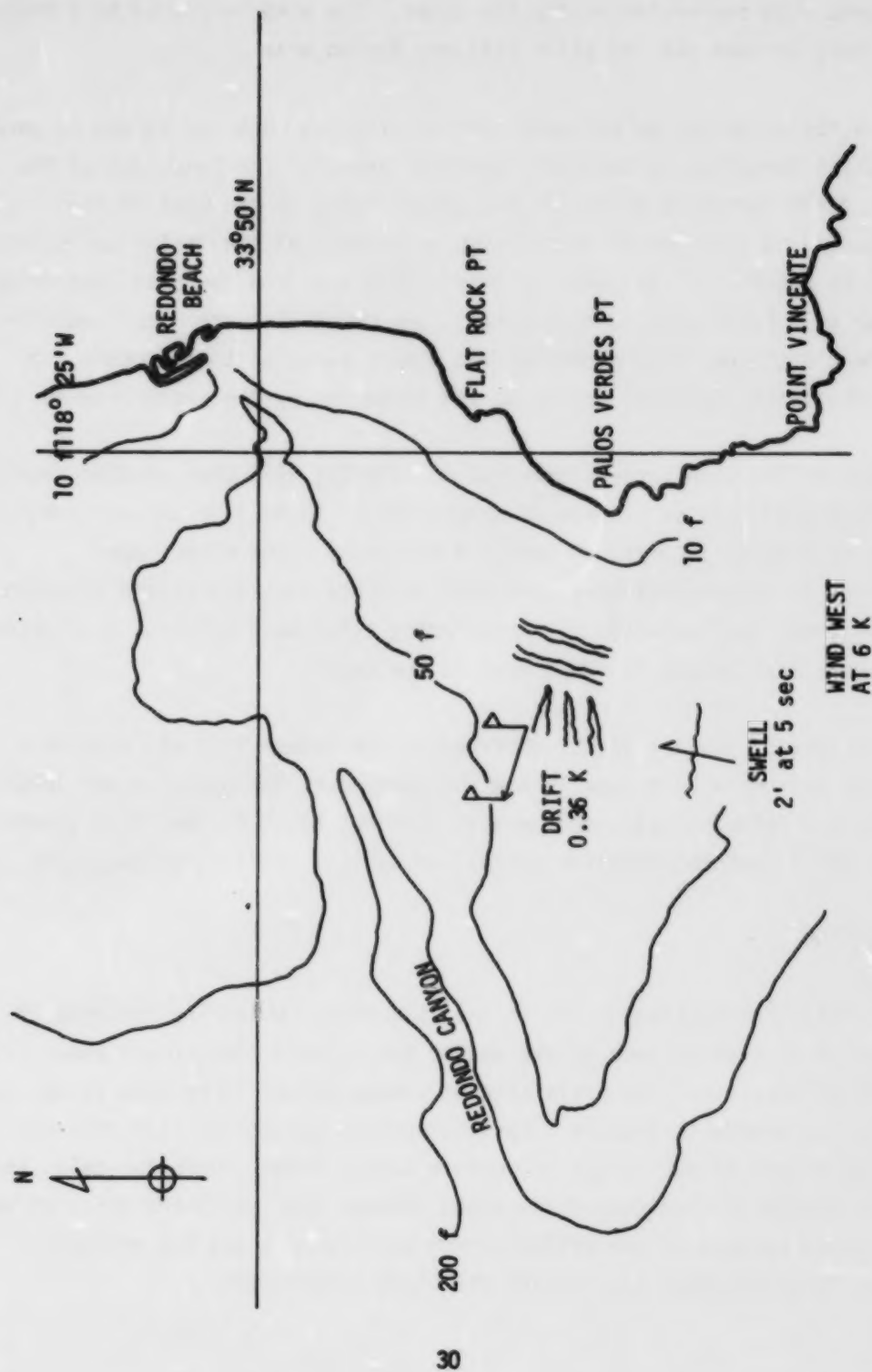


Figure 13. Surface Conditions Off Marineland: July 12, 1973
(Note: Figure 1s only approximate)

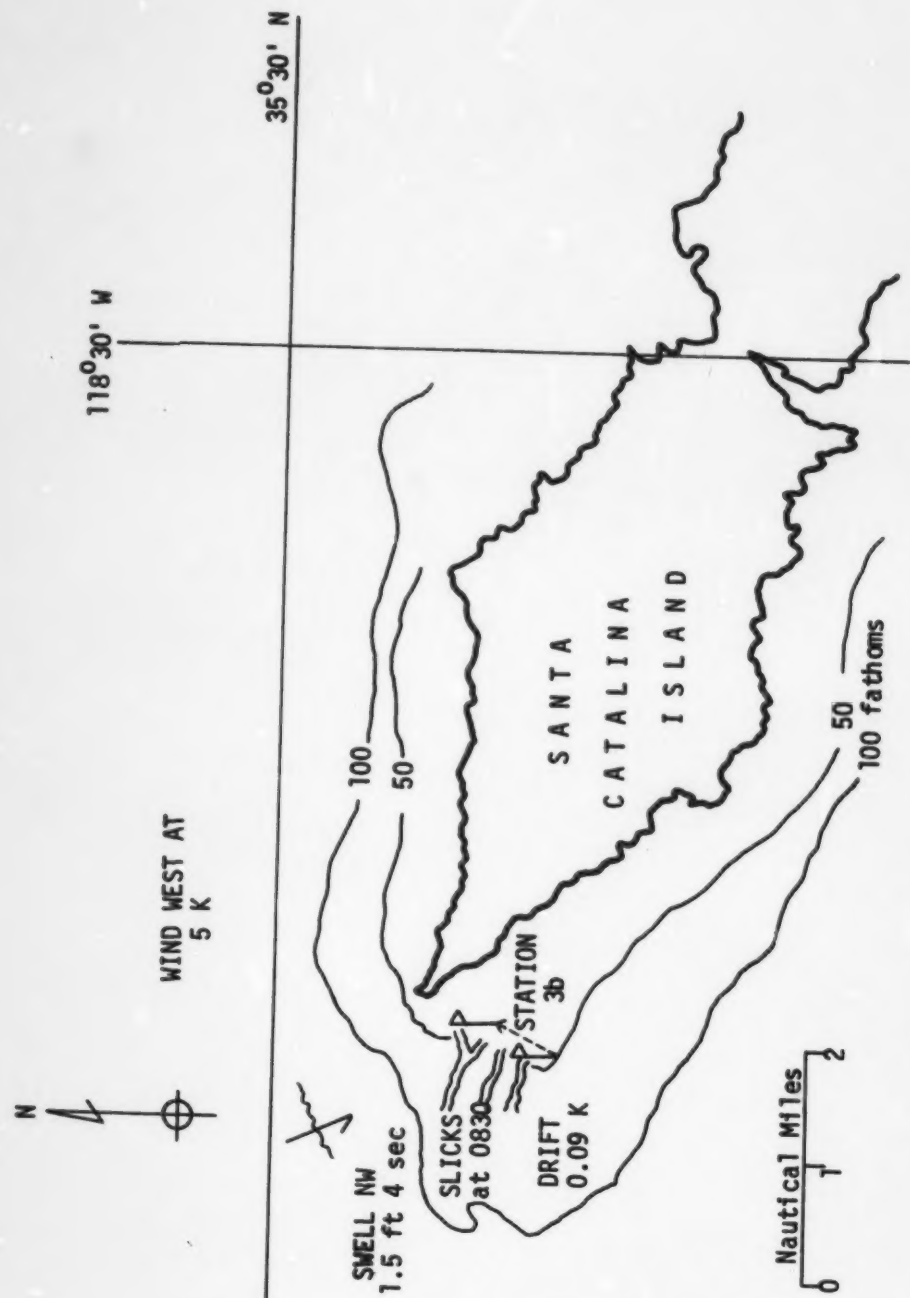


Figure 14. Surface Conditions in Control Area: July 13, 1973

A review of the state of visibility of the sea slicks and wind speeds recorded in this study indicates that the slicks became invisible when the wind was less than approximately 1/2 to 1 m/s. Speeds in excess of 5 to 6 m/s quickly destroyed the slick patterns and formed surface mixing cells in accord with the concepts of Langmuir [4].

The wind seldom permitted the sea surface in the Southern California Bight to attain any state of equilibrium. Strong winds mixed the surface flotage with the upper ocean layer, and once they ceased the flotage reformed. Winds with speeds of 3 to 4 m/s may not disrupt a slick pattern quickly but if given sufficient time the evidence indicates that the slicks will eventually disappear. Finally, a non-surfacing wastewater plume may form a sea slick if the thermocline is located sufficiently close to the ocean surface (approximately 12 m for an outfall releasing 6.2 l/s of effluent per meter of outfall diffuser length).

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V. TRAWLED PARTICULATES

Floating particulates greater than 0.5 mm in size were collected by straining an ocean surface layer approximately 3 cm deep and 0.87 m wide through a 500 μ pore size nylon screen fastened behind a trawling device. The characteristics and dimensions of the trawl used in this study are shown in Figure 16.

The trawl was towed alongside the sampling craft at approximately 0.8 m/s (1.5 knots). At the termination of a trawl the screen was removed from the plastic cod and stored in a petri dish under refrigeration until ready for analysis. The types of analyses conducted on the particulates varied from survey to survey but included at times, 1) type, size, and number of particulates captured; 2) total dry weight; 3) hexane extractable materials (HEM) and the composition of the HEM in terms of fatty acids (FA), pesticides, and polychlorinated biphenols (PCB); and 4) coliform bacteria.

The type, size, and number of particulates were determined visually underneath a dissecting microscope. The HEM were obtained by extraction with hexane in a soxhlet apparatus and the fatty acids by reacting the hexane extracts with α -bromo-2,3,4,5,6-pentafluorotoluene (BFT) to form fatty acid esters. The esters were then determined quantitatively by techniques of gas-liquid chromatography. The PCB and some pesticide compounds were first separated from the HEM with the aid of an activated silica column, then measured quantitatively in a gas-liquid chromatograph. The details of these chemical methods of analyses are presented in Appendix B.

Unfortunately it was not possible to measure the coliform bacteria in a trawl sample without destroying the sample. Such samples were first homogenized in a blender and then filtered through membrane filters in accord with the techniques described in Standard Methods [5]. For this reason the coliform samples had to be collected and analyzed independently of all the other analyses.

DESCRIPTION OF TRAWLS

The extent of each trawl is listed in Tables 3 and 4. Conditions at the time of trawling are described briefly below.

April, 1971

All trawling at the Hyperion outfall was performed within the standing slick shown in Figure 7. The trawling at Station 2, 3.7 km to the north, was undertaken during a period of increasing wind. The slicks were destroyed at that site before the final two trawls could be made. In the control area (Station 3a) all the trawls except the last were made in the large slick lying in the lee of Santa Catalina Island.

August-September, 1971

In this survey the trawls were duplicated as much as possible at a given site with one being taken for coliform bacteria analysis and the other for all the remaining analyses deemed necessary.

The trawling over the Hyperion outfall was commenced in the afternoon when the wind was relatively strong. The sea slicks, ill-defined at best, were destroyed as the trawling progressed. The trawls were conducted progressively eastward commencing over the center of the Y diffuser and ending 700 m to the east. The data shown in Tables 3 and 4 are listed in that order. At Station 2, 3.7 km to the north, trawling was conducted during a period of relative calm.

No slicks were observed over the JWPCP outfalls during the 1971 survey. The order of trawling, as listed in Tables 3 and 4, was progressively westward commencing near the seaward end of the L diffuser (see Figure 10). Three of the four pairs of trawls were taken parallel with the L diffuser and the last west of the Y diffuser. Trawls in the control area (Station 3b) were made during a period of well-defined sea slicks.

July, 1973

No trawls were collected for coliform bacteria analysis during this survey. All trawling was conducted in the morning when some rather ill-defined slicks

Table 3. SUMMARY OF SURFACE TRAWLS
One m² of Trawl Equals 30 $\pm$ of Strained Water

Location	Sta. No.	Date	Trawls			Counts		Dry Wt. mg/m ²	HEM mg/m ²	Fatty Acids			Aesthetic Rating ^a
			No.	Area m ²	% in Slicks	No./m ²	% Sewage Type			mg/m ²	% C ₁₆	% C ₁₈	
Hyperion outfall	1	IV-7-71	3	116	100	5.2	92	12	2.8	0.001	36	42	3
				268	100	3.4	82	5.7					
				163	100	18	89	44					
		VIII-31-71	4	70	30	0.37	78	0.15	0.06	0.001	36	42	
				74	30	0.78	94	0.95	0.39	0.27	22	73	
JWPCP outfalls	4	IX-3-71	4	73	0	1.2	82	2.4	0.91	0.22	27	67	2
				62	0	1.4	93	25.3	6.6	0.80	26	52	
				35	none	0.80	46	0.46	0.15	0.01	32	53	
		VII-11-73	4	118	none	0.75	41	4.7	0.15	0.02	29	61	
				101	none	3.4	85	36	2.8	0.01	31	39	
Hyperion, 3.7 km N	2	IV-7-71	3	108	none	9.0	91	9.0	4.4	0.66	16	79	2.3 1.5
				245	100			24	12	1.1	21	76	
				318	20			51	32.5	2.8	34	61	
		IX-1-71	4	231	20			26	9.0	1.1	25	68	
				276	20			6.6	1.7	0.10	27	67	
Hyperion, 3.7 km N	2	IV-7-71	3	304	48	0.93	61	1.4	0.89				
				320	none	0.55	49	1.0	0.11				
				320	none	0.30	37	0.13	0.021				
		IX-1-71	4	110	100	0.88	56	0.94	0.15	0.05	64	31	
				159	23	0.36	83	0.38	0.10	0.01	31	61	
Hyperion, 3.7 km N		IX-1-71	4	148	100	1.5	73	2.6	0.07				
				58	43	1.6	99	1.7	0.31	0.01	42	44	

Table 3 (continued). SUMMARY OF SURFACE TRAWLS

Location	Sta. No.	Date	Trawls			Counts		Dry Wt. mg/m ²	HEM μ g/m ²	Fatty Acids			Aesthetic Rating ^a
			No.	Area m ²	% in Slicks	No./m ²	% Sewage Type			μ g/m ²	% C ₁₆	% C ₁₈	
JWPCP, 14 km NW	5	VII-12-73	4	162	N.R.			0.36	27	0.36	58	34	1.0
				213	N.R.			0.29	38	4.6	47	48	
				170	25			0.22	16	2.7	47	46	
				263	25			0.50	54	1.1	38	54	
Control Areas, Santa Catalina Is.	3a	IV-8-71	4	200	100	0.20	5	3.6	24				
				200	100	0.96	10	8.5	73				
				106	100	0.22	18	0.13	22				
				526	6	0.13	1.5	0.024	8				
	3b	IX-2-71	4	391	60	0.054	26	0.25	0.1	0.009	67	33	
				314	40	0.070	14	0.59	3	0.078	40	36	
				229	100	0.13	3	3.3	1160	2.0	100	0	
				242	50	0.10	4	0.44	0.6				
	3b	VII-13-73	4	161	N.R.			6.0	3.4	0.43	48	40	
				187	10			2.3	4.6	0.72	46	36	
				220	10			1.4	0.4	0.068	62	27	
				263	N.R.			0.033	1.0	0.087	47	34	

Note: N.R. means not recorded.

^aAverage of judgments of aesthetic appearance made by the sampling crews. The higher the rating number, the poorer the appearance (see Table 7).

Table 4 . SUMMARY OF SURFACE TRAWLS - COLIFORM BACTERIA
One m² of Trawl Equals 30 l of Strained Water

Location	Sta. No.	Date	Trawls			Coliform Bacteria	
			No.	Area m ²	% in slicks	No./m ²	No./100 ml
Hyperion outfall	1	IV-7-71	1	26.6	100	150,000	500
		VIII-31-71	4	161	30	1,400	5
				161	30	2,500	8
				74	0	6,700	22
				49	0	3,000	10
JWPCP outfalls	4	IX-3-71	4	70	none	130,000	430
				105	none	43,000	140
				95	none	74,000	247
				195	none	41,000	137
Hyperion, 3.7 km N	2	IV-7-71	1	114	22	6,450	22
		IX-1-71	4	129	100	19,000	63
				252	none	260	1
				160	100	11,000	37
				184	35	1,300	4
Control areas, Santa Catalina Is.	3a	IV-8-71	1	232	100	none	
	3b	IX-2-71	4	533	30	none	
				304	40	none	
				242	100	none	
				350	50	none	

were visible. The first trawl listed in Table 3 for the JWPCP outfalls station was taken 400 m north of the seaward end of the L diffuser, the second parallel to the L diffuser, and the remaining two over the Y diffuser. Trawls taken at the remaining two sampling stations were always made normal to the band slicks visible at the time.

RESULTS OF SURVEYS

Visual Typing

Tables 3 through 5 of Appendix A give the numbers of each type of particulate captured in the trawls made in 1971. Some types seemed likely to be of

wastewater origin; consequently, they were called "sewage types." Included in this category were such objects as pieces of grease and wax, plastic, fiber, rubber, wood, seeds (several kinds), and unidentifiable tissue and debris. The grease and wax particulates were always predominant, and the seeds and plastic were usually prevalent.

Other types of particulates were obviously of natural origin. Pieces of kelp and tar were the most prevalent in this category. In some samples the kelp predominated over all the other types of particulates.

The particulates captured in the August-September survey of 1971 were measured with the aid of a dissecting microscope and the size distributions of the more prevalent types were determined. The mean sizes of each type showed some tendency to vary from location to location but the trends were not pronounced except in the case of the kelp. Consequently, all of the size data except kelp were lumped together without regard to sampling location, with the results shown in Table 5 and Figure 17.

Two types of size distributions were obtained; log-normal and uniform. The sizes of the grease and wax particulates, the tar, and the kelp were distributed log-normally; implying a process of natural erosion [6]. The seeds and pieces of plastic were more or less uniform in size although an occasional large piece of plastic was recovered.

The side netting and collector screen used in the surface trawl had a pore size of 0.5 mm; consequently, it might be expected that objects less than 0.5 mm would not be captured. Generally this proved to be the case but Figure 17 shows that 15% of the grease and wax particulates captured had sizes equal to or less than 0.5 mm. Some of these particulates were very sticky, and they tended to adhere to everything in sight. They seemed to favor the kelp, and in some instances the kelp had grown partially or even completely around the grease. This proves that their association did not always result from the sampling method utilized, and that those particulates had persisted for some time in the environment. It also

Table 5 . CONCENTRATION AND SIZES OF PREVALENT TRAWLED PARTICULATES
(no./100 m² trawled)

Particulate type	Hyperion outfall		JWPCP outfalls	Hyperion, 3.7 km N		Control areas		(Summer, 1971 only) Particulate size ^c	
	IV-7-71	VII-31-71		IV-7-71	IX-1-71	IV-8-71	IX-2-71	Median mm	Mean mm
<u>Sewage types</u>									
Grease & wax	573	60	234	16	52	0.48	<0.08	1.0	1.3
Seeds	85	7.4	11	7.0	20	0.29	0.08	(All 2 to 3 mm)	10
Plastic	4.4	4.7	88	0.3	1.0	0.10	0.25	(Most 2 to 5 mm)	50
Other	54	9	9	8.4	4	1.8	0.53		
<u>Natural</u>									
Tar	32	4.0	13	1.7	3.5	1.8	0.84	1.5	1.9
Kelp	22	0.3	23	1.7	16	14	0.51	2.5 ^a 7.5 ^b	4.0 ^a 16 ^b

^aAt Hyperion, 3.7 km N for IX-1-71.

^bAt JWPCP outfalls.

^cThe mean is the arithmetic mean.

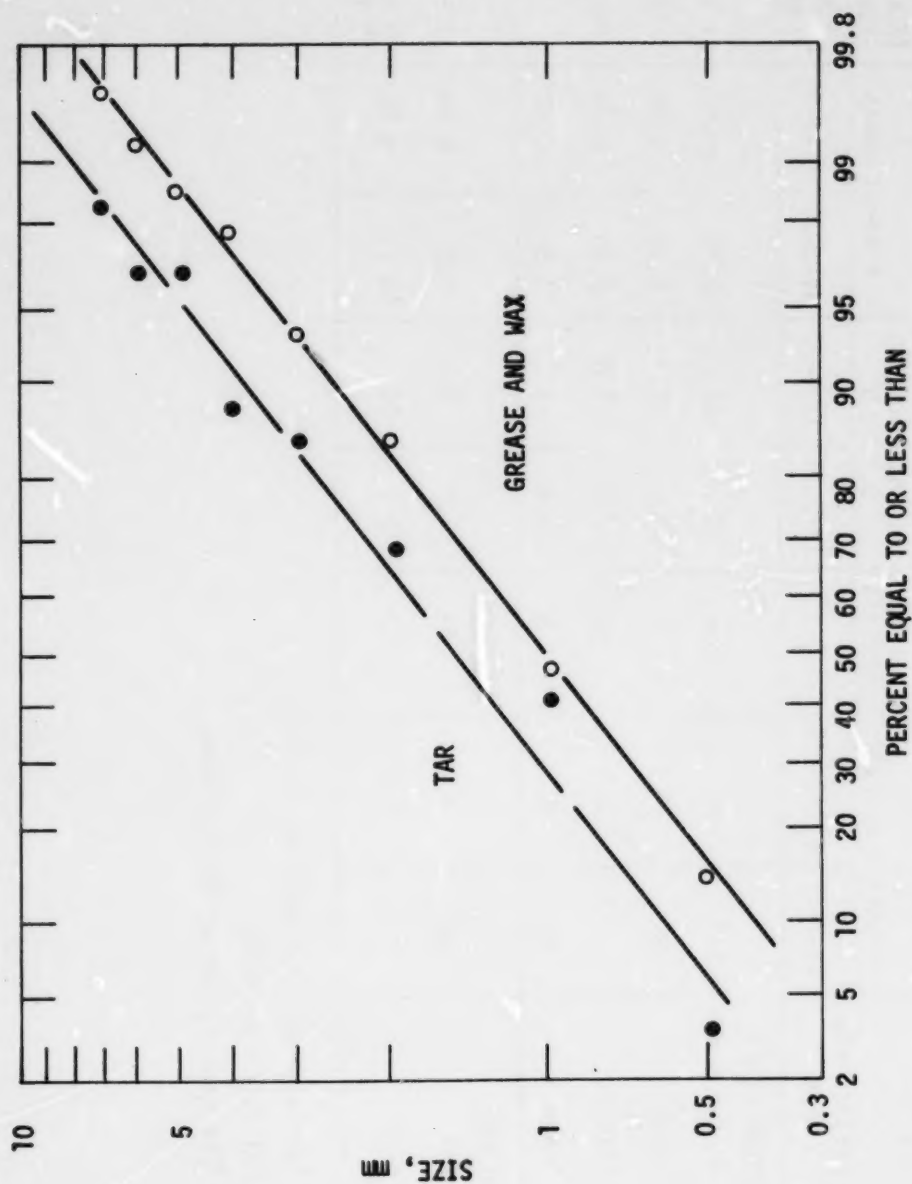


Figure 17. Cumulative Frequency Distribution of Grease and Wax, and Tar Particulates: August-September, 1971.

indicates that the growth of the kelp was not particularly hindered by the adhering grease.

Graphs like Figure 17 have to be interpreted with care. It might be assumed that the tar pieces were generally larger than the grease and wax particulates on the ocean surface. This may not have been the case because the small tar pieces may have slipped through the trawl screens without difficulty whereas the grease and wax particulates tended to stick to the apparatus or other debris, as described above. If 15% of the tar pieces equal to or smaller than 0.5 mm in size had stayed in the collector the two size distributions would have been identical.

In summary, Table 5 shows clearly that the grease and wax particulates captured in the 1971 surveys were predominant in the samples collected over the outfalls and north of the Hyperion outfall. Natural types such as tar and kelp dominated the samples taken in the control areas. The table also shows that the mean size of the grease and wax particulates captured in the summer survey of 1971 was 1.3 mm, and that the largest particulate had a length of 10 mm. Most of the plastic pieces ranged from 2 to 5 mm in size but pieces up to 50 mm in length were taken on occasion.

Dry Weight, HEM, and Fatty Acids

Table 3 summarizes the results of these analyses. The fatty acid analysis was not conducted on the particulates collected in the first survey of 1971, and the degree of unsaturation was not determined until 1973. The significance of these analyses will be discussed in detail subsequently.

PCB and Pesticides

A few samples collected in the August-September 1971 survey were analyzed for PCB and pesticides. Aroclor 1254 was detected in one sample collected over the Hyperion outfall, but it amounted to only 0.13% of the HEM found in that sample. PCB was not detected in any of the other samples tested and it had to amount to less than 0.10% of the HEM in any of them since

that was the limit of detectability for PCB at that time. These fractions were disproportionately small in comparison to those found in the ocean film materials and the analysis was not pursued further. Pesticides, if present, also were minute. These tests were not conducted on the non-extractable particulates such as plastic.

PROOF OF WASTEWATER DERIVATION OF PARTICULATES

Proof that some of the trawled particulates were derived from wastewater discharges is as follows:

1. The particulates could be seen rising to the ocean surface within the vicinity of the marine outfalls. Photographic evidence is presented in Figure 18. (See page 119)
2. Coliform bacteria were found in the particulates collected over and near the outfalls, but not in the control area.
3. Figure 19 shows that the fatty acid compositions of the particulates collected over the JWPCP outfalls on July 11, 1973 and those screened from the JWPCP wastewater effluent on July 13, 1973 were nearly identical; whereas the acid compositions in the Marineland and control areas were grossly different. For example, the proportion of unsaturated C_{18} acids decreased from approximately 60% in the effluent particulates to 25% or less in the control area particulates, and the proportion of C_{16} acids increased from approximately 30% in the effluent particulates to 65% in the control area. (See page 119)

Table 6 presents data pertinent to Figure 19. It shows that the average concentration of HEM strained from the JWPCP effluent on July 13, 1973 was 0.65 mg/l. Both the HEM and the total fatty acid concentrations decreased about 5000 times from the outfall area to the control area. Not all this decrease may be ascribed to the wastewater discharges because the natural background may have been higher close to the mainland.

The fatty acid composition of the HEM was also determined in the samples collected in the August-September survey of 1971 but the degree of

Table 6
EXPLANATION OF FIGURE 19
FATTY ACID COMPOSITION OF LARGE PARTICULATES

Bar no.	Location	Date	No. of observations	HEM	FA	% FA
(1)	Strained JWPCP effluent	VII-13-73	5	0.65 mg/l	0.12 mg/l	18
(2)	Over JWPCP outfalls	VII-11-73	4	15 mg/m ²	1.3 mg/m ²	9
(3)	14 km NW of JWPCP outfalls	VII-12-73	4	36 µg/m ²	2.2 µg/m ²	6
(4)	Control	VII-13-73	4	2.1 µg/m ²	0.29 µg/m ²	14

unsaturation was not determined. Otherwise, those results were nearly identical in all respects to those presented and discussed above.

MEASUREMENT OF SURFACE POLLUTION

Several different analyses were used in this study to evaluate the surface flottage. The best means of measuring these particulates derived from wastewater effluents is discussed below.

Visual Typing

The grease and wax particulates correlated fairly well with other non-extractable "sewage types" as shown in Figure 20. The rapid drop off in grease and wax particulates with low concentrations of the other types indicates that either the grease and wax particulates did not spread as far as the other types, or the other types had sources other than wastewater discharges. The figure indicates a natural background of non-extractable "sewage types" in the order of one particulate every 100 to 1000 m².

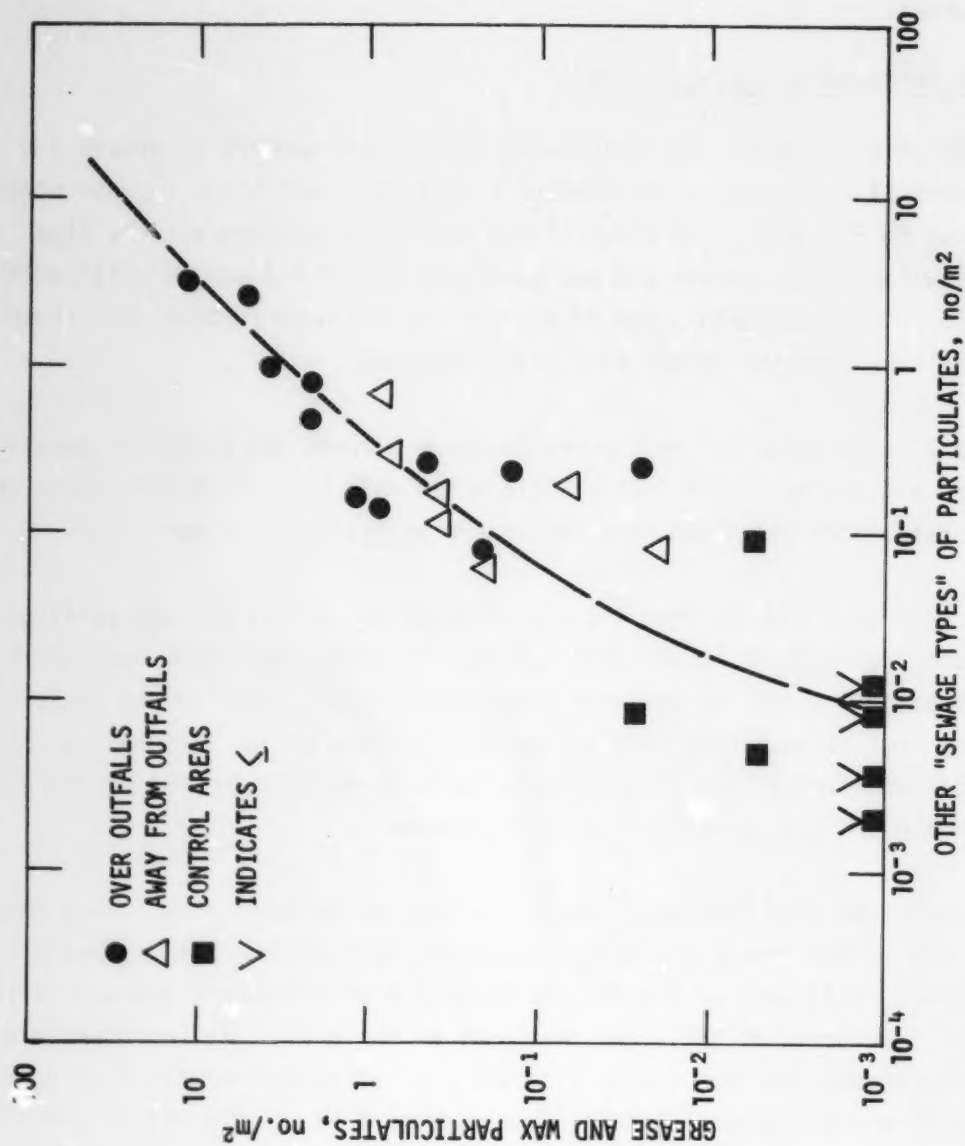


Figure 20. Comparison of Grease and Wax Particulates with Non-Extractable Sewage Types

From this it was deduced that most of the particulates classed as sewage types correlated well with each other. Because the concentrations of these types were much higher over the outfalls than elsewhere (see Table 5) it may be safely assumed that most of them were derived from the wastewater discharges.

Hexane Extractable Materials (HEM)

The HEM of the samples correlated closely with the numbers of grease and wax particulates found in the samples in all cases where tar was not excessive as shown in Figure 21. At first glance this is surprising but the size distribution of the grease and wax particulates did not vary significantly from location to location, and if most of the HEM were derived from those particulates then the correlation should be good.

Figure 21 also shows a 1 to 1 correspondence between the number of particulates and the mg of HEM. This would arise only if most of the grease and wax particulates dissolved into the hexane as explained below:

Table 5 shows that the mean size of the grease and wax particulates was 1.3 mm. Their mean volume, therefore, must have been on the order of 1×10^{-3} ml and with a specific gravity close to one their mean weight must have been on the order of one mg per particulate. Consequently, a 1 to 1 ratio would be obtained only if most of the grease and wax was dissolved by the hexane.

The significance of Figures 20 and 21 should not be overlooked. They show that most of the grease and wax was probably derived from the wastewater discharges, that most of the HEM was derived from the grease and wax particulates (exclusive of tar), and that most of the grease and wax dissolved into the hexane and that there is possibly a background threshold of non-extractable particulates classified as "sewage types." The HEM is, of course, relatively easily determined in a soxhlet apparatus.

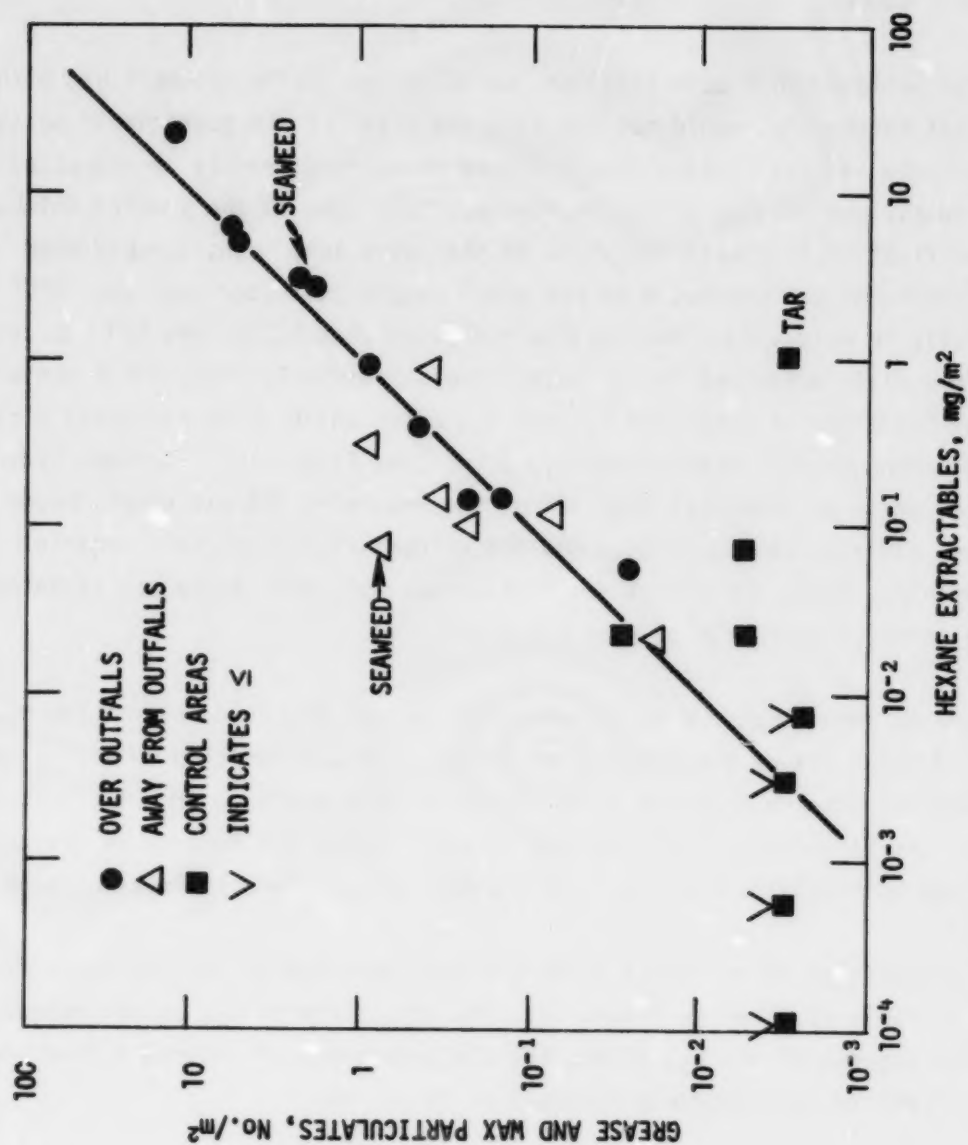


Figure 21. Comparison of Grease and Wax Particulates With HEM

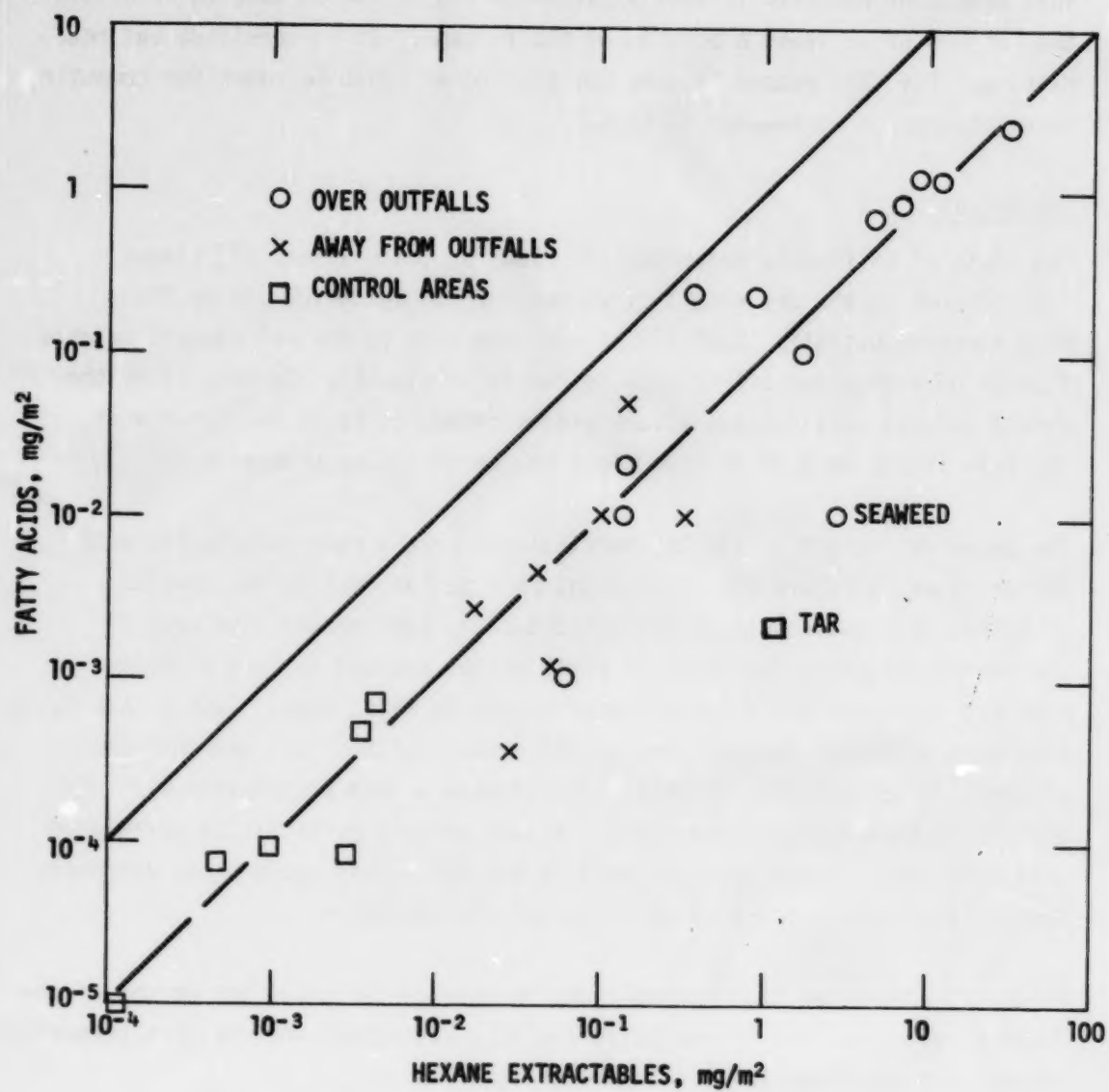
Fatty Acids (FA)

The fatty acids (C_{12} - C_{22}) were determined directly on the HEM without acidification or saponification. Only free fatty acids could be determined in this manner.

It was believed that acidification, which is not easily accomplished with soxhlet extraction, would not increase the yield of HEM appreciably because the grease and wax particulates appeared to extract readily as discussed previously and because little residue was left over in the soxhlet thimble. Saponification increased the yield of the fatty acids considerably when an experiment was conducted on one trawl sample collected over the JWPCP outfalls in July 1973. The results indicated that 12% of the HEM was composed of free fatty acids and 18% of fats. The saponifiable fatty acids contained large fractions of saturated C_{16} and C_{15} acids while those extracted directly were preponderantly unsaturated C_{18} acids (see Figure 19). Carbon, hydrogen, oxygen analyses indicated that 38% of the remaining HEM was simply bound water, 21% alkanes (paraffins) and 10% unidentified long chain organic compounds. Thus, the visual description was apt, the sewage particulates were composed primarily of grease and wax.

Figure 22 shows that the total weight of the unsaponified fatty acids comprised about 10% of the HEM on the average. This proportion varied rather grossly at times but no trend was evidenced with distance from the outfalls. Thus, the FA analysis could be used as well as the HEM to measure the grease and wax particulates but the results would be considerably less reliable.

The composition of the fatty acids altered considerably with distance from the outfalls as shown in Figure 19. The proportion of C_{16} acids increased at the expense of the C_{18} acids, but the proportion of saturated free stearic acid remained approximately constant at 10 to 20%.



Coliform Bacteria

This method of analysis is easily performed and it can be used to ascertain the origins of at least a portion of the flotage. It is sensitive but not precise. For this reason it does not provide an adequate means for computing mass balances on wastewater flotage.

Dry Weight

The State of California Water Quality Plan for Ocean Waters [7] places restrictions on the dry weight of wastewater flotage which can be found over a marine outfall. Such limits are necessary to control non-extractable flotage of wastewater origin such as rubber or plastic. In this study the grease and wax particulates always predominated, so it is not known what the safe limits on such objects might be, aesthetic or otherwise.

The total dry weight of all the particulates gave a poor correlation with HEM as shown in Figure 23. This might be expected because the samples contained varying amounts of non-extractables, some natural and some of wastewater origins. The types of particulates classed as "sewage types" were not separated and weighed independently in this study. Such a task would have been difficult because some of the grease particulates were extremely sticky. It appears that if this had been done a good correlation with HEM would have been obtained because the grease and wax particulates correlated well with other sewage types as well as the HEM. This would be an extremely onerous task and is not advised in normal circumstances.

Figure 23 also shows that commonly nearly half of the total dry weight of the flotage collected over the outfalls could be extracted, whereas this proportion became very small and erratic in the control regions.

Recommendations

These studies indicate that HEM is by far the best analysis for ascertaining the extent of surface pollution created by floating particulates having sizes greater than 0.5 mm. The source of the HEM can be checked by the following

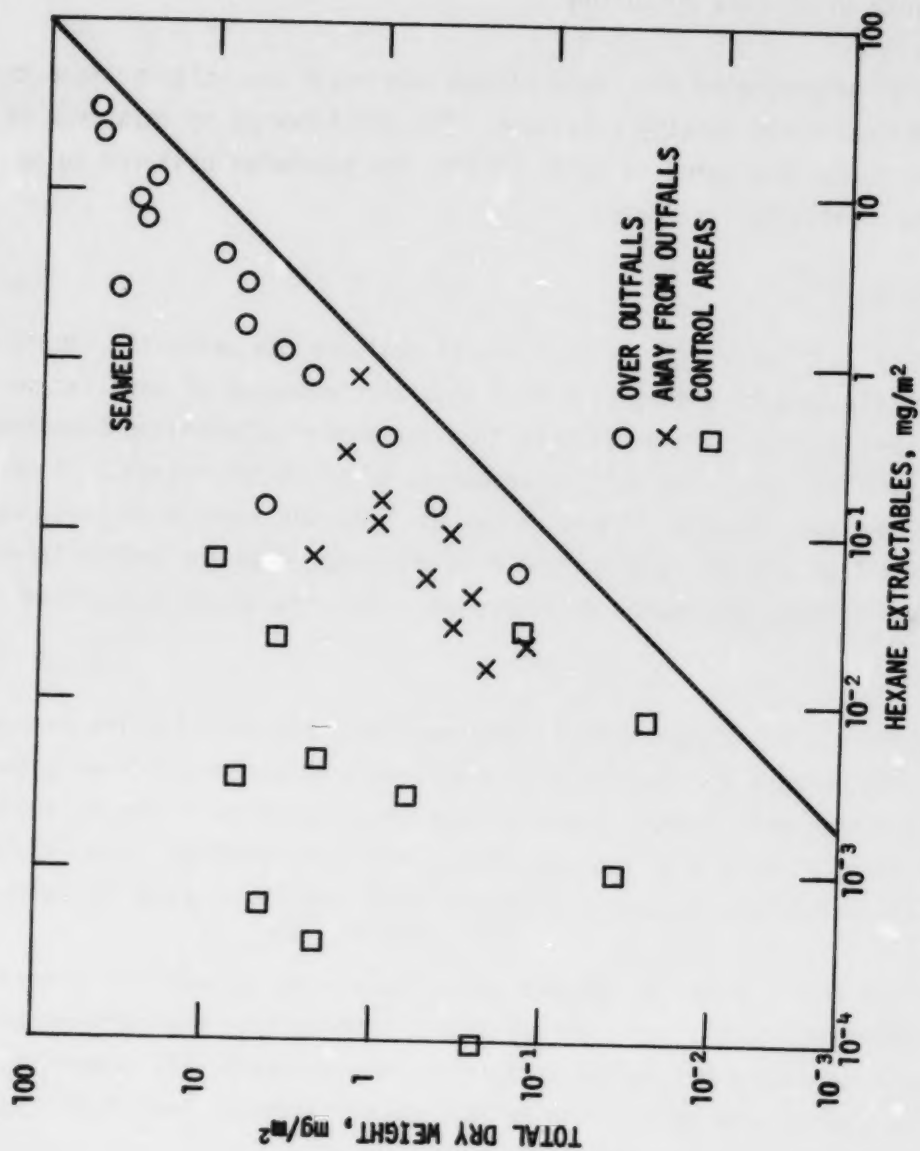


Figure 23. Comparison of Total Dry Weight With HEM

additional analyses; visual identification, fatty acid composition, and coliform bacteria. In the case where non-extractable wastewater particulates are preponderant, a dry weight analysis might prove to be of greater benefit.

SIGNIFICANCE OF SURFACE POLLUTION

It has been demonstrated that particulates can reach the ocean surface through a well defined ocean density structure. The significance of this type of pollution is now evaluated in terms of HEM, the parameter believed to be of greatest value in its control.

Aesthetic Impact

In the July 1973 survey it was possible to evaluate the aesthetic impact of the particulates with a team of 6 to 7 observers composed of sampling personnel and the ship's crew. (Prior to this time the number of sampling personnel was too small to make very valid assessments of aesthetic impact.) A rating sheet of the type shown in Figure 24 was used and the average response was determined from a scale ranging from 0 to 3 points, with the points increasing as the surface appearance deteriorated. The results are summarized in Table 3.

It is difficult to relate surface appearance with any quantitative measure such as HEM because the particulates seemed more objectionable when gathered in a slick than when free, and any surface trawl tends to strike an average through zones of both high and low particulate concentration. Even so, the aesthetic evaluations tended to correlate with the HEM as shown in Table 7.

Remembering that 1 mg/m² of HEM was approximately equivalent to 1 grease and wax particulate/m², it is apparent that a relatively high HEM concentration is necessary before the surface becomes aesthetically offensive. It may be appropriate to maintain an HEM concentration of less than 3 mg/m² to be on the safe side at all times, however.

	No.:
	Date:
	Time:
OCEAN SURFACE AESTHETIC SURVEY	
Location: _____	
Categories: check one	
0. No pollution - water surface appears to be in virgin condition	_____
1. Trace pollution - some evidence of floating material - not significant	_____
2. Obvious pollution - readily observable amounts of debris - unsightly	_____
3. Offensive pollution - sufficient quantities of pollutants present that you wouldn't go in the water	_____
_____ Recorder	

Figure 24. Example of Aesthetic Rating Sheet for Evaluating Ocean Surface Pollution

Table 7. COMPARISON OF AESTHETIC IMPACT WITH HEM

<u>HEM, mg/m²</u>	<u>Average rating</u>
0.005	0 - Water surface in virgin state
0.050	1 - Some flotage evident but insignificant
3	3 - Offensive (in standing slick over Hyperion outfall, April 1971)
9	1.5 - Flotage obvious and somewhat unsightly
32.5	2.3 - Flotage obvious and unsightly - offensive to some

Bacteria

Table 4 lists the results of the bacterial analyses. All of these analyses were made in 1971 when the effluents were not being chlorinated. An opportunity was missed to evaluate the effect of chlorination when these analyses were eliminated in the 1973 survey.

The bacteria were collected on membrane filters and incubated in differentiating media in accord with Standard Methods [5]. Only typical coliform bacteria colonies were counted and recorded (green metallic sheen) but many more atypical colonies appeared on the filters. The atypical colonies were highly concentrated over the outfalls but a few were found in the samples collected on the northeastern side of Santa Catalina Island (Station 3a) in the spring of 1971. As a result, the control area was shifted to the seaward side of the island in the summer survey where no bacterial colonies of any type developed on the membrane filters.

Figure 25 shows the cumulative frequency distributions of the coliform bacteria surface concentrations found over the various outfalls in 1971. The median values of the surface concentration varied widely, with that observed over the Hyperion outfall in August 1971 being significantly less than the others. All of the trawls of the August-September survey were conducted during periods of high wind, when the sea slicks had been, or were on the verge of being destroyed. Undoubtedly the counts would have been higher during a calm spell when all of the particulates would have been present at the air-sea interface.

The coliform samples were collected and analyzed independently of all the other particulate analyses. Even so, an approximate relationship appears to exist between the coliform organisms and the HEM as shown in Table 8.

Aside from the observations made over the Hyperion outfall in August 1971, the table shows that the number of organisms found per mg of HEM was remarkably consistent in the samples taken over or near the marine outfalls.

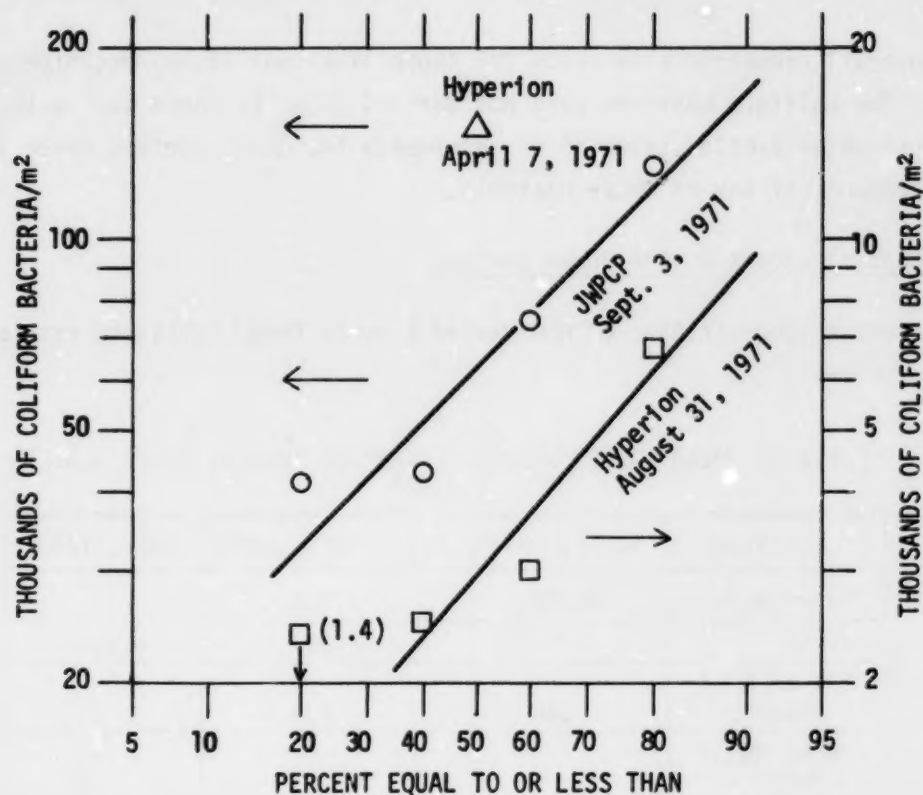


Figure 25. Cumulative Frequency Distributions of Coliform Bacteria Surface Concentration: 1971

Table 8. COMPARISON OF COLIFORM BACTERIA WITH HEM

Location	Date	HEM mg/m ² (average)	Coliform bacteria no./m ² (median)	No./mg of HEM
Hyperion	IV-7-71	10.8	150,000 ^a	1.4×10^4
	VIII-31-71	2.0	3,000	1.5×10^3
JWPCP	IX-3-71	2.2	63,000	2.9×10^4
3.7 km N of Hyperion	IV-7-71	0.34	6,450 ^a	1.9×10^4
	IX-1-71	0.13	2,500	1.9×10^4
(3a)	IV-8-71	0.025	<0.0043 (some atypical)	<0.2
Control (3b)	IX-2-71	0.0012	<0.00070	<0.6

^aOne trawl sample only.

The overall geometric mean value for those areas was 12,000 organisms/mg of HEM. The coliform bacteria were not derived from the ocean bulk water because water samples taken 10 cm underneath the ocean surface never indicated the presence of any of those bacteria.

HEM Concentrations on the Ocean Surface

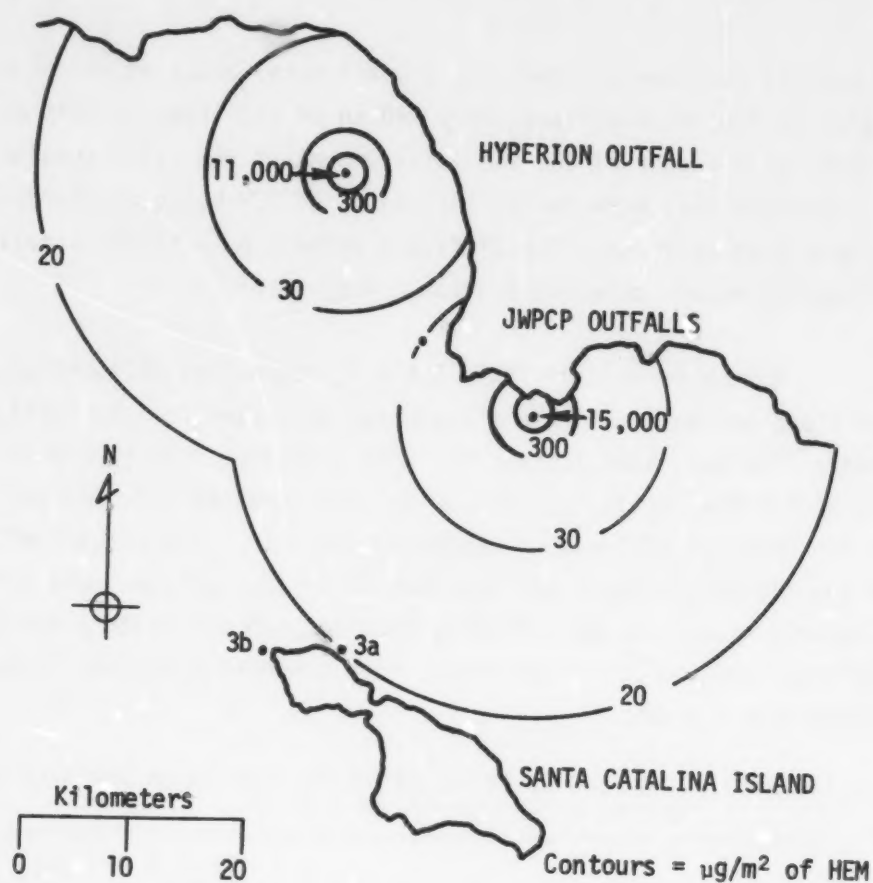
The average concentration of HEM varied grossly from station to station as shown below.

Table 9. MEAN CONCENTRATIONS OF HEM IN TRAWLED PARTICULATES ($\mu\text{g}/\text{m}^2$)

Location	April, 1971	Aug.-Sept., 1971	July, 1973
Hyperion	10,800	2,000	
JWPCP		2,200	15,000
3.7 km N of Hyperion	340	130	
14 km NW of JWPCP			36
Control (3a)	25		
Control (3b)		1.2	2.1

These data are much too few to estimate accurately the total mass of HEM of wastewater origin present on the ocean surface at any given time. Still, it is believed that even a crude estimate is better than none at all, so a concentration distribution of HEM was assumed and the total mass of HEM computed as shown in Figure 26.

The concentration distribution shown in that figure was estimated by subtracting an assumed background concentration of HEM of $5 \mu\text{g}/\text{m}^2$ from the average values presented in Table 9. (The HEM data of Aug.-September, 1971 were not used because of the unfavorable winds existing at the time of sampling.) The zones of highest concentration about the outfalls were arbitrarily assumed to be about 3.5 km in diameter but they could have been much more, or much less extensive than that.



Calculations

HEM conc. $\mu\text{g}/\text{m}^2$	Area (km^2)	Avg. end area (km^2)	Incremental conc. $\mu\text{g}/\text{m}^2$	Incremental weight kg
0	2300			
20	2300	2300	20	46
30	700	1500	10	15
300	90	400	270	108
12,500	20	55	12,200	671
Total				840

Figure 26. Estimate of Mass of Wastewater HEM Present on Ocean Surface - Trawl Samples

The results indicate a surprisingly small total mount of HEM of wastewater origins on the ocean surface, only 840 kg or so. Even if this estimate is in error by a factor of 10, the total amount of HEM still remains small. To comprehend this more fully, the amount of HEM being discharged daily to the area must be known. Two different methods of effluent sampling were employed to obtain this information. They were:

1. In the surveys of 1971, 1.5 l of composited effluent were mixed with clean sea water and the flotage was separated in a specially designed funnel. The separated flotage was then extracted with hexane in a soxhlet apparatus. The details of this method are given in Ref. [8] and the results for the Hyperion effluent are shown in Table 10. The results of this approach are questionable because particulates with sizes greater than 0.5 mm were relatively scarce in the effluents studied, and the flotage derived from a sample as small as 1.5 l could have been composed primarily of particulates smaller than 0.5 mm.

Table 10. ANALYSES OF 24-HR COMPOSITE SAMPLES OF HYPERION EFFLUENT DURING OCEAN SURVEYS OF 1971

Measure	April 6-7 1971	Aug. 30-31 1971
Measured by Hyperion staff		
Grease and oil	12 mg/l	9 mg/l
Suspended solids	64 mg/l	81 mg/l
Vol. suspended solids	50 mg/l	76 mg/l
Coliform organisms ^a		
AM	260,000/ml	430,000/ml
PM	186,000/ml	930,000/ml
Measured by this project staff		
Bulk hexane extractables	10.7 mg/l	8.2 mg/l
Dry weight of floatables	4.8 mg/l	3.1 mg/l
Hexane extractables in floatables	0.15 mg/l	0.30 mg/l

^aDetermined from grab samples.

2. The sampling method was improved in 1973 by pumping a portion of the JWPCP effluent through a screen identical to that used in the surface trawl. The screen approach velocity was 0.8 m/s, the same as used in surface trawling. A maximum of 18 % of the JWPCP effluent could be passed through the screen before serious clogging occurred. The material collected was then extracted with hexane in a soxhlet apparatus. The average HEM concentration of 5 such samples collected through the day on July 13, 1973 is presented in Table 6.

This method could have been improved further by resuspending the captured particulates in clean sea water and separating again in a funnel of the type used in 1971 before extracting with hexane. In this way only those particulates which float in sea water would have been extracted. It is believed that such an improvement would not have altered the results grossly.

The emission rates of HEM from the treatment plants were estimated by multiplying the effluent concentrations of HEM by the plant flows existing at the time of the ocean surveys (Table 2). The results, shown in Table 11, indicate that a metric ton or so of HEM was being released daily to the study area. Comparing this with the mass found on the ocean surface (840 kg) indicates that either the residence time of the particulates on the ocean surface was very short (order of a very few days), or the HEM found in the effluents did not attain the surface. Other alternatives might be a rapid decay in the particulates, which seems highly unlikely because the grease and wax particulates were large and they obviously had persisted for some period of time when stuck to kelp; erosion into smaller particulates missed by the trawl screen; or concentrating in regions not sampled in this study.

To determine if all of the HEM sampled in the plant effluents actually attained the ocean surface a local mass balance was made about the outfalls using the steady state continuity equation in the form

$$Q_w c_w = c U b$$

Table 11. MASS EMISSION RATES OF PARTICULATE HEM FROM TREATMENT PLANTS

Plant	Day	kg of HEM/day
Hyperion	IV-7-71	190
Hyperion	VIII-31-71	390
JWPCP	VII-11-73	880

where Q_w is the effluent flow rate, c_w the concentration of HEM in the effluent, c the concentration of HEM on the ocean surface, U the surface current, and b the width of the diffuser projected normal to the direction of U . The product $Q_w c_w$ is the plant emission rate given in Table 11.

The main problem with this approach is determining U . Surface drogues were used to measure the drift over the outfalls (see Figures 7 to 15) but those drogues were set to a 2 m depth, and experiences of the tracer survey of December 9, 1971 (Figure 11) showed that such drogues did not move with pellets placed on the ocean surface. Even so, for want of better data, the drifts measured by the drogues were used to compute U . These estimates together with computed and observed concentrations of HEM are shown in Table 12.

Considering all the assumptions which had to be made, the agreement between computed and observed concentrations of HEM over the outfalls was good, and the differences were in the right direction (the observed being less than the computed). Some difficulty was encountered in computing the concentration over the JWPCP outfalls in 1973 because the current measured by the drogue was remarkably low (0.11 m/s) which in turn gave a remarkably high computed concentration (114 mg/m²). Obviously if the current was this small, other factors such as plume spread would increase the dispersion and reduce the concentration from that obtained with the continuity equation.

The results of these analyses indicated that most of the particulates screened from the effluents reached the ocean surface. Their residence time on the ocean surface may have been remarkably short, a matter of a day or so. Their

Table 12. LOCAL MASS BALANCE ON HEM OF TRAWLED PARTICULATES

Outfalls	Date	Surface current U		Diffuser length b m	Concentration of HEM, mg/m ²	
		m/s	Direct. true		Calculated c	Observed
Hyperion	IV-7-71	0.17	NNE	1100	12	11 (slick average)
Hyperion	VIII-31-71	0.18	NE	1800	14	6.6 (eastern-most trawl)
JMPCP ^a	VII-11-73	0.11	NW	800	114	32.5 (western leg of L diffuser) 5.4 (avg. over Y diffuser)

^aY and L diffusers considered together.

disappearance most likely was not caused by rapid bacterial decomposition but rather some mechanism of removal from, or transport out of the entire study area. For example, the particulates could have been filtered out on the kelp, consumed by aquatic birds, or transported to the coast by the wind or internal waves. All of these factors were observed in operation during the various ocean surveys.

Transport Study

An attempt was made to measure the movement of large polyethylene pellets (average size of 4 mm and a specific gravity of 0.985) on the ocean surface on December 9, 1971. As usual the weather was not particularly conducive for such work with the wind being onshore and in excess of 3.6 m/s in the morning. This was sufficient to destroy any slicks which might have existed in the study area.

The wind did decrease around 2 pm, however, and band slicks formed in the area as shown in Figure 11. At 2:40 pm, 400 g of the pellets were seeded along 12.5 m of the shoreward edge of a band slick at a density of approximately 900 pellets/m of slick. A surface drogue set for a 2 m depth was also released at that location.

The pellets were followed for a period of 80 minutes and they remained more or less undispersed along the shoreward side of the slick. The slick moved shoreward with an average speed of 0.20 m/s while the wind steadily decreased to values of less than 2.8 m/s. The drogue was not followed but it ended up well southward and seaward of the pellets.

There was a comparatively slight amount of stratification in the water to a depth of 80 m but internal waves were present [9] and the band slicks appeared to be associated with the internal waves. Unfortunately, these observations had to be terminated with the early onset of dusk (5 pm), and it is not clear if the pellets and band slick were being moved shoreward by the onshore wind or the internal waves. Also it would have been interesting to record the fate of the pellets in the surf zone, and if pellets added between the slick bands would eventually be incorporated into one of the slicks.

CONTROL OF SURFACE POLLUTION

The suggestions made herein apply only to the conditions encountered in this study; i.e., primary unchlorinated wastewater effluents submerged beneath an ocean thermocline. Surfacing plumes should give concentrations of particulates at least as great as those found in this study, however. Effects of chlorination on the coliform bacteria contained in the large particulates is unknown but it is likely that the particulates will protect the bacteria from the disinfectant.

Hexane extractable materials (HEM) appear to be the best general analysis for this type of surface pollution. The question remains as to what is a reasonable and safe upper limit for the HEM on the ocean surface. The only measures at hand which could aid in this judgment were aesthetic impact (Table 7) and coliform bacteria (Table 8). Pesticides and PCB compounds were not of great help because their proportions in the particulates were very slight (although foraging aquatic birds might have obtained appreciable doses of the chlorinated hydrocarbons if they consumed enough of the particulates). Fatty acids, fats, and alkanes are benign in the ocean environment, at least at the rates of emission estimated for the large particulates.

The aesthetic ratings given in Table 7 indicated a maximum safe level of perhaps 3 mg/m² of HEM (see p. 54). The coliform data presented in Table 8 were far more difficult to judge, their public health significance being unknown. A commonly accepted standard for ocean bathing waters is less than 1000 total coliform bacteria/100 ml 80% of the time, but a surface concentration cannot be expressed conveniently in terms of a volumetric concentration. For example, the surface trawl used in this study strained the surface water to a depth of approximately 3 cm, but the same particulates would have been captured at a trawl depth of 2 cm or less. Thus, the volumetric concentration increases in proportion with the decrease in the sampling depth considered significant. The depth cannot be considered infinitesimally

small, or there would be insufficient space to hold the particulates. Figure 17 shows that about 99% of the grease and wax particulates captured in 1971 had sizes equal to or less than 5 mm. It was assumed somewhat arbitrarily that a depth less than this would exclude a significant portion of the grease and wax particulates.

It was found that 1 mg of HEM contained a median of 12,000 coliform bacteria (Table 8 and subsequent discussion). Allowing for a depth of 0.5 cm, approximately 4 mg/m² of HEM would give a median volumetric concentration of 1000 organisms/100 mL ($[1000/100 \text{ mL}] \times [5,000 \text{ mL/m}^2] \times [1/12,000/\text{mg}] = 4.2 \text{ mg/m}^2$). Figure 25 shows that the 80% value of the cumulative frequency distributions for surface coliform concentrations was about twice that for the 50% value; consequently, a median of about 2 mg/m² of HEM would be necessary to insure that 1000 organisms/100 mL would not be exceeded in 80% of the samples.

Intuitively, one feels that a coliform standard for floating particulates should be more strict than for the bulk sea water. For example, one grease and wax particulate may contain 12,000 coliform bacteria. This would be equivalent to 1.2 L of seawater at a concentration of 1000 bacteria/100 mL. No individual would swallow 1.2 L of seawater voluntarily, but he might ingest relatively easily a small floating grease particulate. Also, Table 8 indicates that no appreciable coliform die-away occurred in the particulates collected 3.7 km north of the Hyperion outfall. This is not too surprising because the particulates may shield the bacteria and any pathogens present against the rather hostile ocean environment. Some decay must occur but apparently it is much less than that demonstrated for coliform organisms in bulk seawater. Thus, the relatively rapid rate of bacterial decay usually used in ocean outfall design cannot be relied upon in the case of floating particulates.

The results of these studies indicated that wastewater pollution may be detected to concentrations as low as 0.02 mg/m² of HEM (Figure 26). The maximum concentration observed was approximately 33 mg/m² (Table 3). Both the aesthetic ratings and coliform bacteria analyses indicated that a reasonable concentration should be something less than 3 mg/m² of HEM. A

reasonable limit might be 1 mg/m^2 , about 50 times greater than the detectable limit and 33 times less than the maximum concentration observed.

This recommendation may now be compared with the requirements of the California State Water Quality Control Plan for Ocean Waters of California, 1972 (7).

Chapter II A

B. Physical Characteristics

1. Floating particulates and grease and oil shall not be visible.

Floating particulates at the Marineland sampling station (14 km NW of the JWPCP outfalls) were judged visible but not unsightly by the rating panel used in this study (see Table 3). The HEM concentration was only 0.054 mg/m^2 , yet the fatty acid analyses showed that some of the HEM must have been derived from wastewater outfalls (see Figure 19). If taken literally, the above requirement is very strict. Its intent probably was to control gross emissions of floatage of obvious wastewater origin over the outfall diffusers. (Grease and oil slicks are discussed in a subsequent section of this report.)

2. The concentration of grease and oil (hexane extractables) on the water surface shall not exceed 10 mg/m^2 more than 50 percent of the time, nor 20 mg/m^2 more than 10 percent of the time. (The samples shall be taken in the areas of maximum probable impact.)

The method of sampling is not specified in this requirement and in some cases natural surface film concentrations may build up appreciably, necessitating the use of rather liberal HEM limits. This requirement probably was intended to control concentrations of surface film materials. It is nearly useless in controlling large grease and wax particulates, being much too liberal.

3. The concentration of floating particulates of waste origin on the water surface shall not exceed 1.0 mg dry weight/m² more than 50 percent of the time, nor 1.5 mg dry weight/m² more than 10 percent of the time. (The samples shall be taken in areas of maximum probable impact.)

In this study the dry weight of the sewage types generally was not determined separately from that of the natural types. Over the outfalls the HEM represented about 50 percent of the total dry weight when pieces of seaweed, tar, etc. were not prevalent (see Figure 23). The requirement therefore implies limits on HEM about half those stated for dry weight, or about half the level recommended herein for HEM.

If the experiences of this study are valid, the above requirement would be difficult and expensive to enforce with primary effluents because dry weight is not the appropriate analysis for grease and wax particulates, yet they were found to be the predominant sewage type in all of the trawl samples taken during the study. The requirement could be used to control the emission of non-extractable sewage types (plastic, rubber, etc.) but no reasonable criterion can be suggested based on the results of this study because the non-extractable sewage types were encountered relatively infrequently. Obviously the requirement should be rewritten in terms of HEM, not dry weight. Stipulations on dry weight should specify the types of non-extractables to be weighed; making it possible to pick such objects out of the sample and to clean and weigh them without the services of an expert or the expenditure of a great amount of effort.

VI. MICRO-PARTICULATES

SAMPLING PROCEDURE

Nylon netting was used to collect coliform bacteria from the ocean surface. At the request of the Southern California Coastal Water Research Project, who had furnished some of the funds and sampling craft used in the 1971 ocean surveys, the netting was also used to collect samples for neuston (surface plankton). Upon analyzing the neuston samples it was observed that the samples contained debris, some being colored and of an obvious artificial nature. Particulates captured in this manner are called "micro-particulates" in this report.

The nylon netting used in this type of sampling had a two-filament knit with 0.75 to 1 mm openings when purchased new. A sample was obtained by spreading the netting carefully over the water surface and collecting the surface layer into the cloth via capillary action. Being coarsely woven, this netting lost the water collected easily so it had to be lifted from the water surface and inserted into the sample container with great care. Even so, much of the water was lost in the process. Laboratory tests conducted under ideal conditions showed that the netting collected a surface layer averaging 0.1 mm deep from sea water at 22°C when no water was lost from the cloth. This information was used to compute the surface area sampled at sea by dividing the volume of sample collected by 0.1 mm.

The nylon netting was used to collect the coliform bacteria and neuston because the organisms had to be separated from the cloth for further analysis, and laboratory tests showed that this netting released such organisms readily upon repeated washing. The organisms could then be collected on a membrane filter by passing the water released from the cloth together with the wash water through the filter. Samples for coliform bacteria were then incubated in accord with Standard Methods [5] while the neuston and micro-particulate samples were examined directly on the filter with the aid of a microscope.

At first the cloths used to collect the neuston and micro-particulates had an area of 0.4 m^2 but this size proved awkward to handle at sea. All of the cloths were reduced to a uniform area of 0.1 m^2 in the August-September 1971 survey. (The cloths used to collect the bacteria samples were always 0.1 m^2 in area.) Neither coliform bacteria nor micro-particulate samples were collected in the July 1973 survey.

ANALYTICAL PROCEDURE

The resolution employed to count and identify the neuston and micro-particulates in the April 1971 survey was 200X, and approximately 0.3% of the membrane filter area was examined. One sample was collected in slick areas at each station and the average volume of water collected was 36 ml. Thus, the area of sea surface actually examined was approximately 0.0011 m^2 per sample. This gives a least count of approximately 1000 particulates of a given type/ m^2 .

The area of the cloths was reduced to 0.1 m^2 and the magnification increased to 430X in the August-September 1971 survey. In this case the netting was spread over the water surface several times at a given location until a sample volume deemed sufficient was collected. Eight independent samples were collected at most of the stations; four in slick areas and four in non-slick areas. The average volume of water collected per sample was 32 ml, about the same as collected in the April survey.

The proportion of the filter examined was reduced to 0.1% from the 0.3% used in the April survey. Thus, the area of the sea surface actually analyzed was approximately 0.0003 m^2 per sample. The results presented in Table 13 represent the average of four such samples; consequently the actual coverage was approximately the same for both surveys.

RESULTS

The composition and concentration of the micro-particulates varied grossly between the two surveys. The differences in concentration can be explained,

Table 13. COMPOSITION AND CONCENTRATION OF PARTICULATES CAPTURED BY
THE CLOTH SCREEN SAMPLER
(concentrations in thousands/m²)

Location	Type	April, 1971 (200X)						Aug.-Sept., 1971 (430X)				
		No. of obs.	A	B	C	D	E	No. of obs.	D	F	G	H
Hyperion outfall	S	1				46	15	2	6.5	1635	299	
	NS							4	0	328	42	1.7
JWPCP ^a outfalls	S											
	NS							8	2.6	260	21	0.3
Hyperion, 3.7 km N	S	1	37				11	4	1.8	310	20	
	NS							4	3.2	411	30	
Control areas	S	1	1	1	1	1	9	4	0.7	243	30	
	NS							4	5.8	560	35	1.6

^aWindy day

Classification Code:

A	Blue
B	Purple
C	Irradiant
D	Fibers
E	Metallic
F	Clumped or flocculated minute debris
G	Black
H	Other
S	Slick
NS	Non-slick

at least in part, by the differences in magnification employed, but the particulates found in the August-September 1971 survey should also have been observed in the April survey, and vice-versa, because the field coverage was about the same. For example, the large numbers of blue and metallic appearing particulates found in the vicinity of the Hyperion outfall in April 1971 did not appear at all in the samples collected in August-September. The black and clumped particulates observed so frequently in the August-

September survey, on the other hand, were not noticed at all in the April survey.

The particulates forming the clumps of debris observed in the second survey of 1971 were packed too tightly together to permit individual counting or typing. The sizes of the clumps were distributed in a log-normal manner as shown in Figure 27. The size distributions changed from location to location but not from slick to non-slick areas at a given location. The black particulates evidenced similar trends in sizes.

The nylon netting can sample at best only 0.1 m^2 of water surface area. For the analytical procedures used in this study a given type of particulate would have to have a surface concentration in excess of approximately $1000/\text{m}^2$ to be counted. Figure 27 shows that for the prevalent clumps of debris particulates, at least 99% of the particulates were smaller than 100μ . Thus, a gap existed in the sampling and analytical techniques employed in this study to characterize the particulates. Particulates greater than 0.5 mm in size were collected by the surface trawl and those smaller than 0.1 mm and in concentrations greater than $1000/\text{m}^2$ were collected with the nylon netting. Particulates smaller than 0.5 mm and in concentrations less than $1000/\text{m}^2$ generally were missed.

Tables 13 and 14 summarize the results of the micro-particulate studies made in the August-September 1971 survey. The tables show that their concentrations were surprisingly great, and that their average volume/ m^2 may have been greater than that observed for the trawled particulates during the same survey (assuming that the specific gravity of the trawled particulates was close to one). The predominant type of micro-particulate found in the August-September 1971 survey was the clumps of debris. The black particulates were also very prevalent.

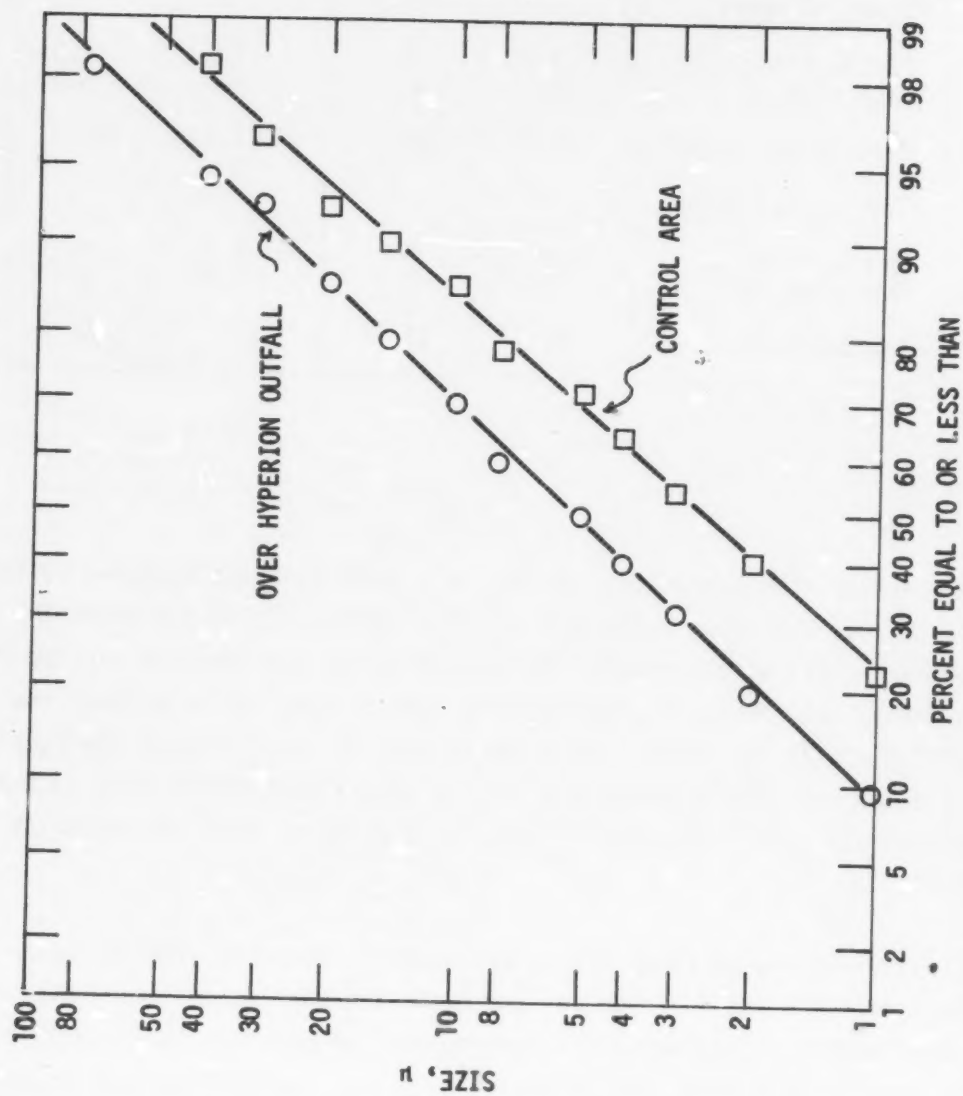


Figure 27. Cumulative Frequency Distribution of Clumps of Debris Collected By The Nylon Netting: August-September, 1971.

Table 14. SIZES OF PREVALENT TYPES OF PARTICULATES CAPTURED BY THE CLOTH SCREEN SAMPLER: AUGUST-SEPTEMBER, 1971

	Hyperion outfall	JWPCP outfalls	Hyperion, 3.7 km N	Control area
<u>Clumps of debris</u>				
Median size, μ	5.5	2.5	3.5	2.5
Mean size, μ	12	6.5	8.2	6.5
Concentration, k/m^2	581	260	363	388
<u>Black particulates</u>				
Median size, μ	4	4	4	3
Mean size, μ	5.5	5.5	5.5	4.1
Concentration, k/m^2	92	21	25	33

The particulates tended to increase in numbers over the Hyperion outfall (Table 14), but those collected over the JWPCP outfalls had about the same concentrations as observed in the control area, and north of the Hyperion outfall. (It should be recalled that samples were collected over the JWPCP outfalls on a windy day.) Again with the exception of the samples collected over the Hyperion outfall, no significant differences in the concentrations of particulates were found between slick and non-slick areas (Table 13).

The sizes of the micro-particulates tended to decrease with distance from the Hyperion outfall (Table 14) but again the samples collected over the JWPCP outfalls contained micro-particulates whose sizes were nearly equal to those found in the control area. No significant differences in particulate size were noted between slick and non-slick areas at a given location.

CONCLUSIONS

The project staff decided to abandon the micro-particulate sampling after the rather inconclusive results obtained in the August-September 1971 survey. Obviously the source of the particulates found in that survey could very well have been atmospheric fallout with the clumped debris being dust blown from the mainland. The ocean surface appeared very clean in the July 1973 survey and possibly micro-particulate sampling conducted at that time would have revealed more about the nature of the micro-particulates. The best that can be stated at this time is that the numbers and volumes of such particulates were gross and it appears that some of them were truly derived from the wastewater effluents as discussed in the following section.

VII. SURFACE SCREEN SAMPLES

SAMPLING PROCEDURE

Surface films have been collected on solid surfaces and metal screens for years. A solid surface dipped vertically through a surface film will collect one coat of film material on the way down and another on the way up. The thickness of the coating will depend on the speed with which the solid is passed through the film and the ability of new film to move into the areas of film depletion. This makes a quantitative estimate of the surface concentration of the film difficult, if not impossible.

Metal screens are an improvement because the closely spaced solid surfaces insure that most of the film contained between the wires will be collected while at the same time they inhibit the movement of new film into the area being sampled. Metal screens have the drawback of not being easily extracted from grease and oil, and they tend to sag from the center no matter how tightly stretched. Cloth screens, first used in this study, could be extracted relatively easily with hexane by folding and inserting into a Soxhlet apparatus. They also tended to conform to the ocean surface and could be handled easily at sea. Their major disadvantage was that most fabrics could not be stripped of their background of hexane extractables even after hours of extraction [10]. Glass fabrics could be cleaned relatively easily, and they were used to collect surface film samples for HEM analysis. The glass cloth utilized had a 0.003-inch (7.6μ) thread diameter, a 40 x 39 warp and fill, and a 2.12 oz/sq yd (72 gm/m^2) weight when purchased new. It was commonly used in the construction of fiberglass boat decks and generally referred to as "deck cloth."

Individual sampling cloths were cut to an area of 0.1 m^2 . The cloths were cut slightly oversized because they shrank slightly when subjected to the initial cleaning procedures. Once cleaned, the cloths released grease and oil collected from the water surface easily, and they were reused until they

unraveled. Their life could have been prolonged greatly by sewing about the edges.

The glass cloth was relatively heavy and closely woven. Water, bacteria, and micro-particulates collected into the fabric were not released easily when washed with water. For this reason the cloth could not be used to collect those samples which required easy release to analyze; i.e., coliform bacteria, neuston, and micro-particulates.

The cloths were applied to the ocean surface with clean wooden tongs and allowed to rest on the surface under their own weight. Clean fiberglass rods were then inserted under the center of the cloths as quickly as possible and they were raised from the surface and rolled about the rods for insertion into individual sample containers. Some water dripped from the cloths in the process but measurements showed that most must have remained in the cloths. The average volume of water held on the 0.1 m² cloths in the July 1973 survey was 12.8 ml with a coefficient of variation of 11%. Laboratory tests indicated a pickup of about 15 ml without rolling, but some of this water could have been excess fluid lying on the surface of the cloth. It appears that the water was bound tightly in the cloth by surface tension and the depth of water sampled may have varied between 0.128 and 0.15 mm.

SAMPLING AND ANALYTICAL ACCURACY

The analytical methods utilized paralleled those employed for the trawled particulates. The glass cloths were first air-dried and extracted with hexane in a soxhlet apparatus without prior acidification or saponification. The long-chain fatty acids (C₁₂-C₂₂) present in the HEM were analyzed by reacting the HEM with the BFT reagent to form fatty acid esters which were then identified and measured quantitatively by techniques of gas-liquid chromatography. The PCB compounds and some pesticides were separated from the HEM in an activated silica column and determined by methods of gas-liquid chromatography.

These approaches measured insoluble duplex films adequately. A vegetable oil composed primarily of unsaturated C_{16} and C_{18} fatty acid esters was dissolved into hexane and spread on clean sea water at 20°C . The hexane was allowed to evaporate and the average surface concentration was computed to be 71 mg/m^2 . The film was sampled with a 0.1 m^2 glass cloth and extracted with hexane. The results indicated a surface concentration of 76 mg/m^2 , within 7% of that computed.

A duplex film is also created in oil spills and is commonly thought of as being surface pollution. Natural sea slicks are formed by films one molecule thick, and such monolayers are not well understood.

Palmitic acid (saturated C_{16}) was added to the surface of distilled, carefully cleaned water employing the classical procedures of Langmuir [11] and Adam [12]. The bulk water had a pH of 5.5 and a stable monolayer was formed having an area of $19.7 \text{ \AA}^2$ per acid molecule (slightly less than the commonly accepted value of $20.5 \text{ \AA}^2$ for any normal saturated fatty acid). The layer was sampled with 0.1 m^2 glass cloths with the reduction in the surface area of the film being measured after each sampling. The reduction in area averaged 0.095 m^2 with a coefficient of variation of 3.7%. This indicates that the cloths consistently collected 95% of the palmitic acid monolayer. Stearic acid (saturated C_{18}) would undoubtedly have behaved in the same way.

The pH of sea water is normally relatively high and only tiny fractions of the fatty acids will remain undissociated in the bulk water phase. Depending on the concentrations involved, the dissociated acids can form insoluble salts with the divalent cations present in the sea water. Magnesium salts probably would predominate because their solubility products are the smallest of all the cations commonly encountered in sea water. Such insoluble salts can move to the water surface to aid in the formation of sea slicks. The stability of fatty acid salt films seems to be dependent on the concentrations and proportions of cations and acids present. Fatty acid salt films are poorly understood and have been investigated little in the past.

In summary, it is believed that the glass cloth sampler collected insoluble duplex and stable monolayer surface films accurately. The divalent acid salts probably were not extracted to any significant extent with the hexane because the samples were not acidified. Alkanes, fats, free fatty acids, alcohols, etc. were extracted to become a part of the HEM but only the free fatty acids were analyzed because the fatty acid esters were not decomposed first by saponifying. Acidification and saponification were not easily performed on the minute quantities of material collected in the cloth screens, and every additional analytical step introduced the spectre of more background contamination. It should also be recalled that micro-particulates were found in great profusion on the sea surface and that they also would be captured by the glass cloth sampler; consequently, it was difficult to assess which portions of the HEM or fatty acids were derived from the surface film and which from the micro-particulates.

RESULTS OF SURVEYS

Hexane Extractable Materials (HEM)

Four individual glass cloth samples were collected at each station in the April 1971 survey. These samples were taken in slick areas only. The sampling was extended to both slick and non-slick areas in the August-September 1971 survey with rather inconclusive results. The sampling frequency was then increased greatly in the July 1973 survey as shown in Table 15.

The table shows that the HEM concentrations were extremely variable and that they decreased grossly on the average from 1971 to 1973. That decrease might have been caused in part by increasing analytical precision in the second year, but it could have stemmed as well from actual seasonal and weather-effects. Some of the HEM concentrations found in the 1973 survey were so low they approached the background levels still existing in the glass cloths (0.10 mg/m² or less). Those particular observations are indicated by dashes in Table 15. (The 1973 observations were corrected for a background of 0.10 mg/m² which stemmed from the glass cloth screens employed.)

Table 15. Concentration of Cloth Screen HEM
(conc. in mg/m²)

Type	Hyperion Outfall		JWPCP Outfalls		Hyperion, 3.7 km N		JWPCP 14 km NW	Control Areas		
	IV-7-71	VIII-31-71	IX-3-71	VII-11-73	IV-7-71	IX-1-71	VII-12-73	IV-8-71	IX-2-71	VII-13-73
Slick	12.60	1.60		0.35	2.10	1.25	0.33	1.30	0.80	0.23
	0.25	2.15		1.50	5.75	0.80	0.40	2.65	0.75	-
	1.40	1.55		1.00	1.20	1.45	1.95	2.80	2.25	0.32
	1.35	3.05		0.40	1.70	3.30	0.54	1.40	1.60	0.29
		0.85		0.64			0.12			0.36
				0.32			0.64			0.38
				0.38			0.47			-
				1.29						-
				0.71						0.15
				3.41						0.23
Non-slick				0.82						0.58
				0.73						0.18
				0.60						0.62
				1.00						0.27
				0.45						
	3.90	1.84		0.91	2.69	1.70	0.64	2.04	1.35	0.26
				0.26	0.12	0.75	-		1.05	
	0.30	0.30	1.45 ^a	0.45		1.40	0.20		3.35	0.40
	1.20	2.12	1.10	0.41		1.05	0.25		1.30	0.16
	1.30	1.30	0.95	0.23		1.85	0.24		-	0.35
Mean			0.50	3.96			0.34			0.06
			2.30	0.60			0.25			0.08
			3.60	1.08			0.47			0.13
			1.50	1.10			0.21			0.13
			0.65	1.03			0.13			0.20
			3.10	0.82						0.25
				0.82						0.12
										0.08
										0.10
										-
Mean		1.23	1.70	0.98		1.26	0.23		1.43	0.16

^aWindy conditions, no slicks present.

^bSee Table 16 for location over diffusers.

Fatty Acids (FA)

Table 16 lists the overall weights of the long-chain fatty acids (C_{12} - C_{22}) found in the cloth screen samples collected in the July 1973 survey. The ranking of the observations is identical to that presented for HEM concentrations in Table 15, so direct comparisons can be made if so desired. No significant background of FA existed in the glass cloth screens.

Fatty acids were not determined on the samples collected in the April 1971 survey and the fatty acid composition was not fully evaluated in the August-September 1971 survey. The average values of total fatty acid concentration found in the latter survey are presented in terms of percent of HEM in Table 17. (The means listed in Table 17 do not always compare with those given in Table 15 because not all of the HEM samples were analyzed for FA.)

Coliform Bacteria

Surface coliform bacteria were collected independently with the nylon net sampler as described previously in Section VI. Bulk water samples for coliform organisms were collected 10 cm underneath the surface screen samples with the aid of a sterile Cornwall continuous pipetting device. The bacteria were separated and incubated on membrane filters in accord with Standard Methods [5]. Bacteria samples were not collected in the 1973 survey.

The screen samples were always taken in slick areas in tandem with the glass cloth samples except in the region of the JWPCP outfalls on September 3, 1971 when no sea slicks were visible. The results of these observations are presented in Table 18.

PCB Compounds

Glass cloth samples collected in a given region were pooled to obtain sufficient HEM to analyze for PCB compounds and pesticides. Small quantities of such pesticides as DDE and DDT were observed frequently but their concentrations were always very much less than the PCB compounds so their magnitudes were not ascertained. The results of the pooled screen samples are presented in Table 19.

Table 16. CONCENTRATION OF CLOTH SCREEN FATTY ACIDS: JULY, 1973
(conc. in $\mu\text{g}/\text{m}^2$)

Type	Over JWPCP Outfalls		JWPCP 14 km NW	Control
	VII-11-73		VII-12-73	VII-13-73
Slick	L	31.0	17.3	5.9
		lost	13.3	1.0
		160.2	73.1	8.6
		47.5	12.1	1.2
		128.2	14.2	15.8
		49.4	8.4	8.9
		26.3	2.4	6.4
	Y	223.0		1.4
		28.1		-
		112.4		1.3
		114.5		1.2
		45.3		3.0
		82.9		6.1
		94.3		2.9
		61.4		
Mean		86	20.1	4.6
Non-Slick	L	20.2	4.7	
		87.3	10.1	12.4
		68.7	20.0	9.7
		27.0	11.4	7.6
		286.7	11.7	3.6
		49.1	14.5	5.8
		100.5	3.1	5.2
	Y	65.8	1.3	1.7
		139.5	-	12.5
		90.5		3.5
		62.5		14.3
				1.8
				5.7
				11.9
Mean		91	8.5	7.4

Table 17. MEAN CONCENTRATIONS OF CLOTH SCREEN HEM AND FATTY ACIDS
(concentration in mg/m²)

Location	Type ^a	April, 1971			Aug.-Sept., 1971			July, 1973		
		No. of Samples	HEM	% FA	No. of Samples	HEM	% FA	No. of Samples	HEM	% FA
Hyperion outfall	S	4	3.9	-	5	1.8	12			
	NS				3	1.5	5			
JWPCP outfalls	S							8	1.13	8.4
	NS							6	0.91	9.3
L	S							6	0.52	14.3
	NS				9 ^b	1.7	14	5	1.06	9.2
Hyperion, 3.7 km N	S	4	2.7	-	4	1.7	14			
	NS				3	1.4	15			
JWPCP, 14 km NW	S							7	0.64	3.2
	NS							9	0.23	3.7
Control areas	S	4	2.0	-	4	1.3	13	14	0.26	1.8
	NS				3	1.9	21	13	0.16	4.6

^aS = slick and NS = non-slick.

^bWindy day - no slicks.

Table 18. CONCENTRATION OF COLIFORM BACTERIA: CLOTH SCREEN
AND OCEAN WATER SAMPLES

Location	Date	Cloth Screenings					Bulk Water ^a			
		No. of Samples	ml ^b Filtered	No. of Colonies	No. / 100 ml	No. / m ²	No. of Samples	Total ml Sampled	No. of Colonies	No. / 100 ml
Hyperion outfall	IV-7-71	4	4.7 4.7 4.5 7.2	41 34 none none	880 720 <22 <14	880 720 <22 <14	4	75	none	<1.3
	VIII-31-71	4	14.9 1.94 10.0 4.8	none 100 none none	<7 5150 <10 <21	<7 5150 <10 <21	4	400	none	<0.25
JWPCP outfalls	IX-3-71	4	5.2 5.4 5.1 5.4	21 none none 30	405 <19 <20 555	405 <19 <20 555	4	400	none	<0.25
Hyperion, 3.7 km N	IV-7-71	4	33.2 total	none	<3	<3	4	100	none	<1
	IX-1-71	4	35.1 total	none	<3	<3	4	400	none	<0.25
Control areas	IV-8-71	4	33.9 total	none	<3	<3	4	200	none	<0.5
	IX-2-71	4	28.8 total	none	<3.5	<3.5	4	400	none	<0.25

^a Collected 0.10 m under ocean surface.

^b ml of sample actually filtered, not m² of sample collected.

Table 19. CONCENTRATION OF CLOTH SCREEN PCB COMPOUNDS
(concentration in $\mu\text{g}/\text{m}^2$ as Aroclor 1254)

(concentration in µg/lit - as Aroclor 1254)

Location		Type ^a	April, 1971			Aug.-Sept., 1971			July, 1973		
			b	PCB	% of HEM	b	PCB	% of HEM	b	PCB	% of HEM
Hyperion		S	1	120	0.96	4	39	2.2			
		NS				3	3.3	0.23			
JWPCP outfalls	Y	S							5	8.7	0.77
		NS							6	4.7	0.52
	L	S							6	2.5	0.49
		NS				9 ^c	3.1	0.18	5	3.2	0.30
Hyperion, 3.7 km N		S				4	5.7	0.36			
		NS				4	5.8	0.44			
JWPCP, 14 km NW		S							7	2.0	0.31
		NS							8	2.1	0.89
Control areas		S	1	<10	<0.83	4	7.5	0.60	12	1.1	0.42
		NS				4	6.4	0.35	12	1.3	0.80

^aS = slick and NS = non-slick.

^bNo. of samples pooled to obtain PCB analysis.

^cWindy day - no slicks.

DISCUSSION OF RESULTS

Coliform Bacteria

The coliform bacteria provided the only direct evidence that some of the flotsam collected by the cloth samplers was derived from the wastewater discharges. Large numbers of coliform bacteria were found at times in the nylon net samples collected over the outfalls in the 1971 surveys, but the results were highly variable with either large numbers being recovered or none, as shown in Table 18. No coliform organisms were found in the

bulk water samples taken 10 cm underneath the screen samples, and any such concentration had to be less than approximately one organisms/100 ml.

The variable nature of the data suggests that the bacteria were contained in fine debris of wastewater origin. The nylon net sampler collected a layer about 0.1 mm deep and the maximum size of the particulates captured was less than 100 μ as shown in Figure 27. It appears that the bacteria containing debris had sizes of less than 100 μ . If they averaged 100 μ then the volumetric concentration of bacteria in numbers/100 ml would be equal to the surface concentration in numbers/m². If they were smaller then the volumetric concentration would be proportionately greater.

Figure 28 shows the cumulative frequency distribution of coliform bacteria found over the outfalls in 1971 in terms of number/100 ml (or number/m²). The frequency distribution was close to exceeding a bathing water standard of 1000 organisms/100 ml for 80% of the time. These concentrations probably would be superimposed on those found for the trawled particulates (Figure 25).

PCB Compounds

PCB compounds as Aroclor 1254 were highly concentrated in the slick areas over the outfalls as shown in Table 19. Extraordinary concentrations of 120 and 39 $\mu\text{g}/\text{m}^2$ were found over the Hyperion outfall in 1971. These would be equivalent to volumetric concentrations of 800 and 260 $\mu\text{g}/\text{l}$, respectively, assuming a sampling depth of 0.15 mm for the glass cloth screens. These appear well in excess of the solubility of PCB compounds in water [13], suggesting that the PCB compounds were dissolved in the film material and/or micro-particulates. With the exception of observations made directly over the various outfalls the PCB fraction of the cloth screen HEM was fairly consistent, averaging about 0.58% by weight. In the trawled particulates, the PCB fraction of the HEM was generally less than 0.10%. The PCB compounds apparently tended to concentrate to a greater degree in the substances collected by the glass cloth samplers than in the trawled particulates.

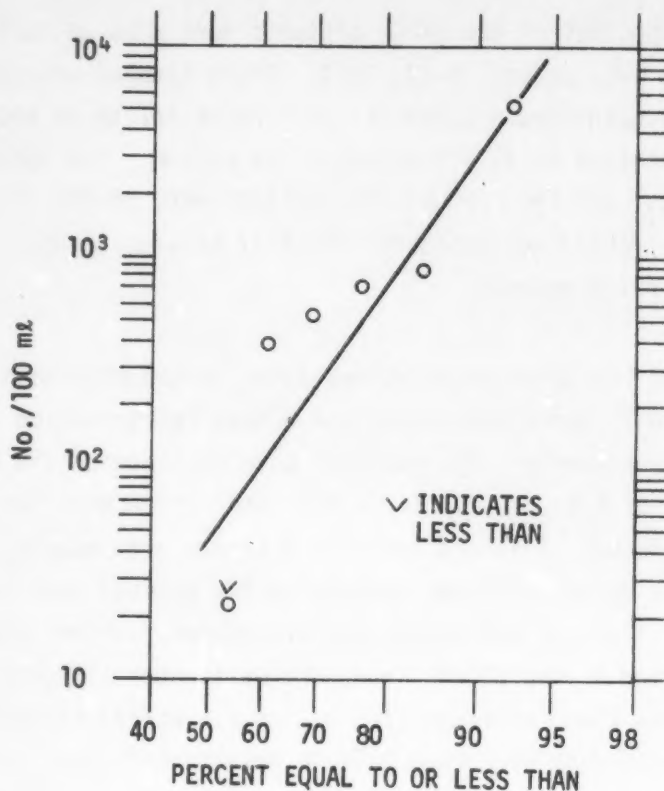


Figure 28. Cumulative Frequency Distribution of Coliform Bacteria Found in Screen Samples Taken Over the Outfalls: April and September, 1971

An appreciable source of PCB compounds could have been atmospheric fallout [1]. The fallout along the coast within the study area might have averaged $0.26 \mu\text{g}/\text{m}^2\text{-day}$ as Aroclor 1254 during the months of June and July 1973 [14]. Information concerning decrease in fallout with distance from the coast was unavailable to this study but DDT compounds decreased by a factor of about 4 from the coast to Santa Catalina Island. Assuming a similar decrease in PCB compounds, the fallout may have averaged approximately 0.5 kg/day on the study area.

Data of the SCCWRP study [14] indicated average concentrations of Aroclor 1254 of $2.0 \mu\text{g}/\text{l}$ or so for the JWPCP effluent during the period July 6-12, 1973, and $0.36 \mu\text{g}/\text{l}$ for the Hyperion effluent during the week of June 18-24,

1973. Daily composites of the JWPCP effluent were also collected for this study during the week of July 6-12, 1973. These samples were acidified and extracted in a liquid-liquid extraction apparatus for three hours with hexane followed by separation on an activated silica column. The output on the GLC column was gross, and the typical PCB patterns were masked by large quantities of unidentified compounds. Further separation and identification procedures were not pursued.

A grab sample of the JWPCP effluent was taken in the afternoon of July 13, 1973 and diluted 17 times with clean sea water, extracted and analyzed for PCB. In this case Aroclor 1254 patterns were distinct on the GLC output and a concentration of 6.5 $\mu\text{g}/\text{l}$ was indicated after correction for dilution and sea water background. This was for only a single grab sample, but the analysis was deemed accurate because of the unusual care taken in the liquid-liquid extraction and separation procedures. Using this concentration and those reported in the SCCWRP study the wastewater effluent PCB mass emission rate was found to range from 3.3 to 9.6 kg/day to the study area, depending on whose data were used. These results indicate that the wastewater mass emission rate of PCB was considerably greater than the rate of atmospheric fallout in the study area.

Four 4.5 l bulk ocean water samples were collected 0.5 m beneath the ocean surface at each station occupied in the 1973 survey. The average results are compared with the surface screen samples in Table 20.

Table 20. COMPARISON OF OCEAN WATER AND SURFACE CONCENTRATIONS OF AROCLOR 1254: JULY, 1973

Location	Bulk Samples $\mu\text{g}/\text{l}$	Cloth Screen Samples		Concentrating Effect
		$\mu\text{g}/\text{m}^2$	$\mu\text{g}/\text{l}^{\text{a}}$	
JWPCP outfalls	0.103 ^b	4.8	32	310
14 km NW of JWPCP	0.025	2.1	13.7	540
Control area	0.018	1.2	8.0	440

^aAssuming a sampling depth of 0.15 m.

^bL diffuser.

The results show that the PCB compounds tended to concentrate strongly on the ocean surface. The concentrating effect remained relatively constant throughout the study area; or in other words, the bulk and screen concentrations of the PCB compounds corresponded fairly closely with each other. In this regard the PCB results differed greatly from those found for the fatty acids to be discussed subsequently.

The average bulk water PCB concentration found over the L diffuser of the JWPCP outfalls was approximately 50 times higher than that reported by SCCWRP for bulk samples collected in the same area at a depth of 3 m in May 1973 [14]. The reason for such a wide discrepancy is unknown except that a more efficient hexane extraction technique was employed in this study.

The approximate computational methods shown in Figure 26 and the data presented in Tables 19 and 20 were used to estimate the mass of PCB present on the ocean surface in the surveys of August-September 1971 and July 1973. The mass computed was 24 and 6.4 kg (as Aroclor 1254), respectively. These results reflect the greater concentration of PCB found everywhere in the study area in the 1971 survey; the cause being unknown but possibly due to restrictions being placed on the use of PCB by the manufacturers after 1970. The July 1973 results indicate a surface residence time in the order of 13 days if the PCB compounds were derived solely from atmospheric fallout.

The presence of significant atmospheric fallout makes it difficult to estimate the proportion of surfaced pollution derived from the marine outfalls. Both the bulk water and surface screen results shown in Tables 19 and 20 indicate that the contribution of the marine outfalls must have been significant, otherwise the appreciable decrease in the PCB concentrations with distance from the outfalls could not be logically explained. For this reason the PCB results were taken as a second proof that some of the substances collected by the glass cloth screens were derived from the wastewater discharges.

HEM and Fatty Acids

The HEM and fatty acid results were much less amenable to analysis than were the PCB or coliform results. The variations were so great it was difficult to judge if the differences found in average concentrations were truly significant. When a sufficient number of observations were taken, the differences proved significant as shown in Figure 29 for the HEM concentrations found in the slick and non-slick areas of the control station in July 1973.

The HEM and fatty acid concentrations did decrease markedly with distance from the JWPCP outfalls in the July 1973 survey as shown in Table 17. No such pronounced decrease was observed in the August-September 1971 survey. Again the causes of this are unknown. In nearly all cases the observed HEM concentrations were surprisingly low in sea slick areas.

A free fatty acid occupies approximately $20.5 \text{ \AA}^2$ of surface area in a stable monolayer. Palmitic acid, for example, would produce a surface concentration of 2.08 mg/m^2 as HEM under such circumstances. Most of the observed HEM and fatty acid concentrations were much lower than this.

To understand the role of wastewater fatty acids in the formation of sea slicks, 2 x grab samples of the JWPCP effluent were collected on July 13, 1973 and added to an aluminum pan containing clean sea water. The effluent was added in sufficient quantity to give an overall sea water dilution of 18, about 5 times less than that being achieved over the outfall diffusers. The depth of the diluted effluent in the pan was 17 cm and the pan had a surface area of 0.224 m^2 . The contents of the pan were agitated gently with magnetic stirrers and six cloth screen samples were taken at approximately 20 minute intervals of time after an initial waiting period of about one hour. Bulk samples were taken from the undiluted effluent and from the pan mixture after completion of the surface screening and acidified. Surface tension was also measured during the course of the experiments. The results of one such experience is presented in Table 21 and discussed in detail below, with the results of all the experiments being essentially the same.

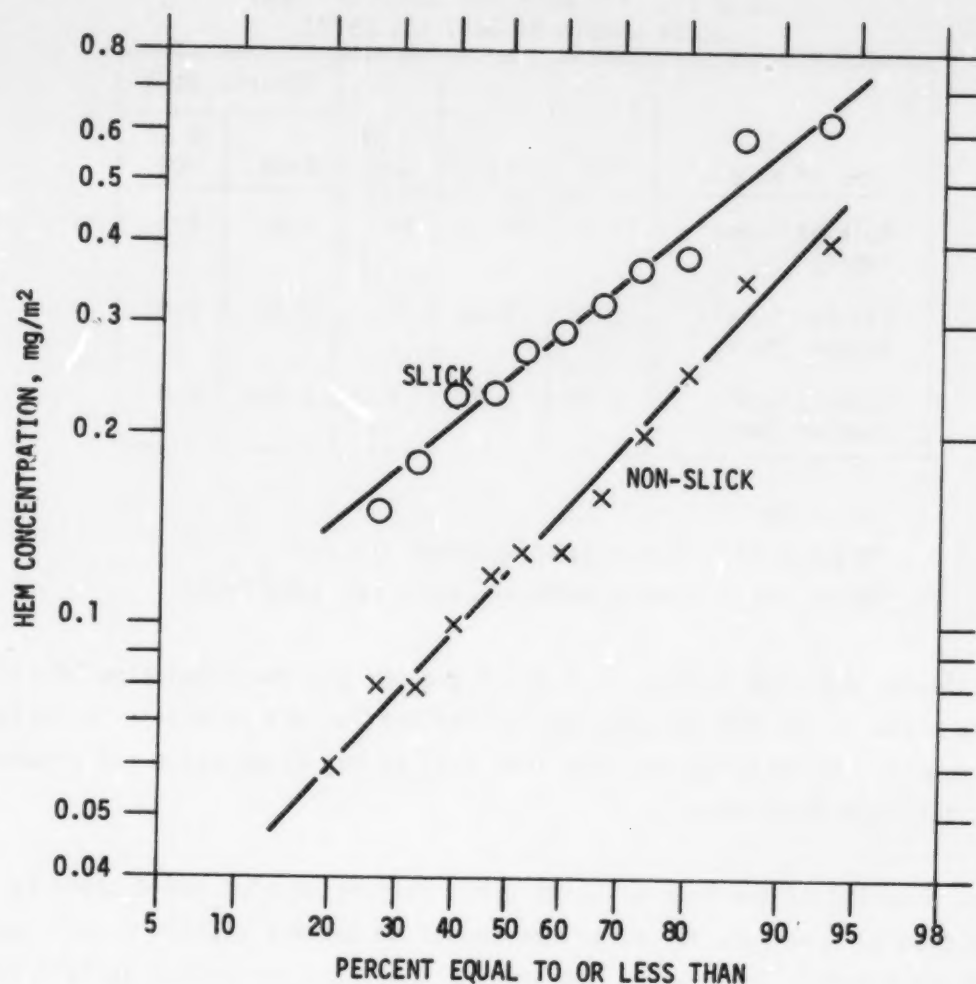


Figure 29. Cumulative Frequency Distribution of HEM Found in Cloth Screen Samples in Control Area: July, 1973

The concentration of stearic acid (saturated C_{18}) was 5.8 mg/l in the bulk effluent sample, or 8.1% of the total HEM. This includes the salts of the acids because the sample was acidified before extraction. The concentration of the acid in the pan after dilution should have been approximately 0.32 mg/l instead of the 0.15 μ g/l observed. It appears that some of the stearic acid salts had migrated from the mixture before the onset of pan screening.

Table 21. PAN DATA FOR JWPCP EFFLUENT
(grab sample of July 13, 1973)

Type of sample	HEM	FA	% of HEM	Stearic acid	
				Conc.	% of HEM
Bulk effluent ^a (mg/l)	71.4	29	41	5.8	8.1
Diluted bulk ^{a,b} in pan (mg/l)	2.36	0.48	20	0.15	6.4
Glass cloth ^c samples (mg/m ²)	1.49	0.10	6.7	0.030	2.0

^aAcidified.

^bDiluted 17:1 with clean sea water.

^cMeans for 6 cloth samples - cloths not acidified.

The stearic acid was reduced to 6.4% of the HEM and the proportion of all the fatty acids in the HEM was reduced from an initial 40% to 20% in the diluted pan sample. In other words, more than half of the fatty acids had disappeared from the diluted mixture.

After a period of one hour of waiting the surface tension had dropped by more than 20 dynes/cm, far more than needed to depress capillary waves and form sea slicks. The glass cloth samples indicated an average surface concentration of HEM of only 1.5 mg/m², and the concentration of stearic acid was only 30 µg/m². By this time the acid comprised only 2% of the HEM extracted from the glass cloths. The glass cloths were not acidified prior to extraction, and the acid salts would not be extracted with the hexane. It is probable that appreciable quantities of the acid were missed in this way, but exactly how much cannot be estimated from a mass balance because some of the salts went to the sides of the pan as well as the water surface, and because new film formed quickly after a cloth sample was taken from the water surface. Indeed it appeared as if surface sampling could have been continued indefinitely with significant HEM recovered until all

of the film forming substances had been removed from the pan.

It is possible that the method of sampling and analysis employed to measure the surface films altered the fatty acid-salt relationships actually existing at the air-water interface. For example, the cloths were air-dried prior to extraction and the sea salts would concentrate as the water evaporated. This could produce additional fatty acid salts depending on the pH of the evaporating solution.

In summary, it appears that the ocean fatty acid salts were not extracted from the screen samples and it may have been that additional salting-out occurred during the air drying stage. The recovery of saturated long-chain free fatty acids should be very small therefore, as indicated by the results of the effluent sampling experiments.

Figure 30 and Table 22 show the mean compositions of the fatty acids found in the screen samples collected during the July 1973 survey. Palmitic acid predominated in all areas sampled and stearic acid was relatively prevalent. The concentrations of both of those acids decreased grossly with distance from the JWPCP outfalls, with stearic acid decreasing some 20-fold from the outfalls to the control area. The proportion of stearic acid found in the HEM decreased from 1.4% over the outfalls to only 0.33% in the control area.

Table 22. FATTY ACID COMPOSITION OF CLOTH SCREEN SAMPLES: JULY, 1973^a
(concentrations in $\mu\text{g}/\text{m}^2$)

Location	HEM	FA	% of HEM	Palmitic acid	Stearic acid	
					Conc.	% of HEM
JWPCP outfalls	910	88	9.6	27	13	1.4
14 km NW of JWPCP	410	13.6	3.3	5.2	1.9	0.46
Control area	210	5.9	2.8	1.9	0.69	0.33

^aWeighted means of the data presented in Table 17.

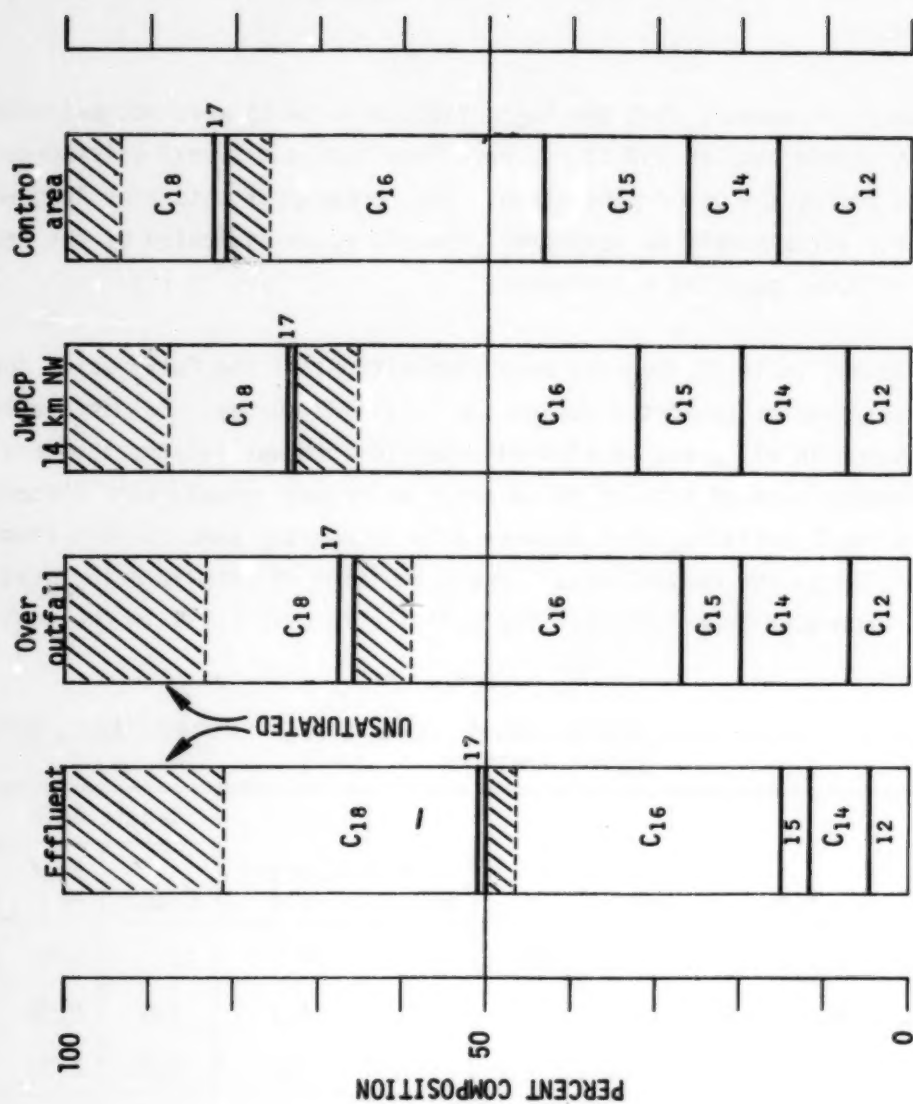


Figure 30. Fatty Acid Composition of Cloth Screen Samples: July, 1973

Bulk ocean water samples collected 0.5 m underneath the surface were also analyzed for HEM and fatty acids with the average results being shown in Table 23. Those samples were acidified at the time of collection.

Table 23. FATTY ACID COMPOSITION OF BULK OCEAN SAMPLES: JULY, 1973^a
(concentrations in $\mu\text{g}/\ell$)

Location	HEM	FA	% of HEM	Palmitic acid	Stearic acid	
					Conc.	% of HEM
JWPCP outfalls (L diffuser only)	54	6.4	12	2.7	0.92	1.7
14 km NW of JWPCP	51	9.1	18	3.6	0.92	1.8
Control area	31	3.3	11	1.1	1.1	3.6

^aSamples taken 0.5 m beneath ocean surface and acidified for preservation.

The table shows that the bulk water concentrations of palmitic and stearic acid were nearly constant in the study area during the July 1973 survey. Stearic acid had an average concentration of only 1 $\mu\text{g}/\ell$ or so, and palmitic 2.5 $\mu\text{g}/\ell$. Even so, a water depth of only one or two meters would be sufficient to produce a fatty acid slick at those concentrations if the acids could attain the water surface. A direct comparison cannot be made between the acids found in the bulk water and in the screen samples because the bulk samples were acidified and the screen samples were not.

The change in the fatty acid composition of the cloth screen samples with distance from the JWPCP outfalls in the July 1973 survey tended to parallel that noted for the trawl particulates captured at the same time (Figures 19 and 30). The major differences were a greater proportion of the lighter acids and a smaller proportion of unsaturated C_{18} acids in the screen samples.

ORIGINS OF CLOTH SCREEN FATTY ACIDS

It appears that the fatty acids found in the unacidified and unsaponified screen samples may have been derived primarily from micro-particulates rather than surface film materials. Some of the reasons for this belief are as follows: the surveys of 1971 showed that micro-particulates were profuse and of significant volume, and that the coliform bacteria were distributed in a spotty manner; the free fatty acid concentrations found at a given site were highly variable but almost always too small to form a sea slick; differences in fatty acid concentrations between slick and non-slick areas were usually relatively minor; the acidified bulk water palmitic and stearic acid concentrations were fairly constant in the study area, implying that their surface concentrations (either free or as salts) should be reasonably uniform, but the surface concentration of stearic acid decreased 20-fold from the JWPCP outfalls to the control area; and the methods of analysis employed might make any free stearic acid very scarce unless protected by being incorporated in some type of micro-particulate.

THE SIGNIFICANCE OF THE SURFACE POLLUTION

The coliform bacteria and PCB analyses demonstrated clearly that some surface wastewater pollution existed in the study area. The PCB data could not be used to trace that type of pollution because of interferences derived from atmospheric fallout. Only the fatty acid data could be used to obtain such an estimate, and then only very crudely.

Of all the fatty acids recovered from the ocean surface stearic acid will salt out the most readily and possibly be the most persistent in the marine environment. Assuming that this acid was derived primarily from wastewater micro-particulates and that it was relatively inert inside the micro-particulates, the mass of HEM of wastewater origin could be estimated grossly. Obviously these assumptions are highly questionable. For example, free stearic acid could have been contained in the particulates falling from the atmosphere but no information on such a phenomenon was available.

Tables 21 and 22 show that the stearic acid proportion of the HEM decreased from 2.0% in the effluent pan samples to 0.33% in the control area. Assuming that the stearic acid proportion would have been 2.0% over the JWPCP outfalls if all of the HEM had been derived from wastewater micro-particulates, the following ratios of wastewater HEM to total HEM are observed.

Table 24. ESTIMATED CONCENTRATION OF HEM OF WASTEWATER ORIGINS IN CLOTH SCREEN SAMPLES

Location	Proportion of wastewater origin	HEM ($\mu\text{g}/\text{m}^2$)	
		Wastewater origins	Background
Over JWPCP outfalls	0.75	690	230
14 km NW of JWPCP	0.22	90	320
Control area	0.16	34	177

Using this information and the computational methods shown in Figure 26, the mass of HEM in the study area was estimated to be 312 kg, or about the same order of magnitude as the HEM derived from the trawled particulates.

The surface materials collected by the cloth samplers proved of polluttional significance in terms of the PCB compounds and coliform bacteria as well as the above. All of the remarks made in Section V concerning the coliform bacteria found in the trawled particulates apply here as well, only more so, because the particulates carrying the bacteria were much smaller ($100\ \mu$ or less in size) and generally more dispersed on the ocean surface.

CONTROL OF SURFACE POLLUTION

The requirements of the California State Water Quality Control Plan for Ocean Waters of California [7] specify that the concentration of hexane extractables on the water surface shall not exceed $10\ \text{mg}/\text{m}^2$ more than 50% of the time, nor $20\ \text{mg}/\text{m}^2$ more than 10% of the time. The methods of sampling and analysis were not specified. It was decided in Section V of this report that this requirement was much too liberal to control adequately trawled grease and

wax particulates of sewage origins, and that it probably was intended to control concentrations of surface film materials.

Table 15 shows that only one cloth sample out of the many taken had an HEM concentration in excess of 10 mg/m², and even a primary effluent diluted 17 times with sea water produced a surface concentration of only 1.49 mg/m² after an hour of agitation (Table 21). An HEM concentration of 10 mg/m² can be encountered only with: 1) a chance encounter with a large grease and wax particulate, or 2) a duplex film. It represents very gross surface pollution indeed.

The HEM analysis, as performed in this study, proved not to be a sensitive measure of the pollution collected by the glass cloth screens. Coliform bacteria and massive concentrations of PCB compounds were found over the outfalls at HEM concentrations ranging from 0.9 to 3.9 mg/m² on the average, and a similar range in HEM concentration was observed in the control areas (0.16 to 2.0 mg/m²). Also, the HEM concentrations tended to vary grossly from survey to survey, indicating either a poorly developed method of analysis or unknown seasonal effects.

It could be that further development of analytical methods (cloth sample acidification, for example) would improve the reliability of the HEM determination. A few experiments on cloth acidification (data not shown) indicated that the HEM may not be increased grossly, however, although the fatty acids increased appreciably.

If the HEM analysis cannot be used to control the type of pollution collected by the cloth screens (except in the case of duplex films) then the question remains as to what type of measure might be appropriate. Free stearic acid may indicate micro-particulate pollution but little experience has been obtained with this measure and the analysis is not easily performed. The coliform bacteria analysis, however, is both definitive and easily performed and the results can be judged to some extent in terms of their pollutional significance. Considering the accessibility of this type of pollution to the

public, it seems logical to restrict the surface bacteria to concentrations of 1000 organisms/100 ml or less as total coliforms, or 1000 organisms/m² assuming a sampling depth of 0.10 mm with the nylon netting screens. This might raise havoc with present ocean outfall disposal methods, necessitating the disinfection of the entire effluent prior to release even when the effluent plume is well submerged beneath the ocean thermocline. Also, it is not known if the bacteria present in the micro-particulates would be killed even with effluent disinfection, and it may be that even a disinfected surfacing secondary effluent plume would not meet this requirement. For these reasons the requirement suggested above for coliform bacteria is offered with considerable trepidation.

PCB concentration requirements could also be established, regardless of the source of the compounds. These investigators are unable to judge what an environmentally safe level of such compounds might be at the ocean surface. Concentrations on the order of one mg/l as Aroclor 1254 appear excessive, however, and such a level was approached in some samples collected over the Hyperion outfall in 1971.

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IX. GLOSSARY

Band Slicks - Long, narrow sea slicks running parallel with each other.

Floatables or Flotage - All foreign substances collected from the water surface by the sampling devices developed herein.

Grease - A general term used to designate the hexane extractables found in domestic wastewater or in a polluted sea slick.

Langmuir Cell - One pair of alternating (right and left) series of longitudinal vortices at the water surface with their horizontal axes parallel to the wind. Generally such vortices are produced at wind speeds in excess of 3.4 m/sec.

Micro-Particulates - Microscopic particulates captured by the nylon netting sampler. Generally these particulates were less than 100 μ in size.

Slick - Flotage so concentrated that capillary waves are dampened visibly (or the surface tension is depressed significantly). A slick may contain the surface film material proper, particulates, plankton, debris, froth, foam, etc.

Surface Film - A collection of foreign molecules on the water surface.

Trawled Particulates - Particulates larger than approximately 0.5 mm in diameter collected by the trawl net.

APPENDIX A

MISCELLANEOUS TABLES

Table 25. OCEAN CURRENTS AT HYPERION OUTFALL
(6:20 to 7:14 a.m., April 7, 1971)

Depth m	Speed knots	Bearing Mag.
0-1	0.30	360
10	0.42	180
20	0.30	320
30	0.25	300
40	0.15	Rotating
50	0.07	Reversing
60	0.12	90

Table 26. OCEAN CURRENTS IN AUGUST-SEPTEMBER 1971 SURVEY

Station 1 (7 to 8 a.m., Aug. 31)			Station 2 (10 to 11 a.m., Sept. 1)		Station 3b (9:40 to 10:15 a.m., Sept. 2)		Station 4 (7:41 to 8:21 a.m., Sept. 3)	
Depth m	Speed knots	Direction true	Speed knots	Direction true	Speed knots	Direction true	Speed knots	Direction true
1	.30	N	.25	W	.20	W	.40	NW
10	.15	SW	.30	W	.20	NW	.20	N
15	.15	SW	.35	W	.20	E	.25	NW
20	.20	SW	.15	NW	.05	NW	.20	N
30	.20	SW	.10	N	.20	E	.30	N
40	.25	SW	.20	SW	.10	N	.20	N
50	.10	W	.25	SW	-	-	.20	NW
55	-	-	.10	SW	-	-	.10	N

Table 27. DESCRIPTION OF TRAWLED PARTICULATES: OVER OUTFALLS
(no./100 m² trawled)

Trawl No.	Station 1							Station 4			
	IV-7-71			VIII-31-71				IX-3-71			
	1	2	3	1	3	5	7	2	4	6	8
<u>Sewage Types</u>											
Grease and wax	380	233	1270	2.5	46	85	111	14	23	213	557
Seeds	43	27	209		12	6.9	11	5.7	0.9	6	27
Misc. tissue	31	2.6	69			2.7				5	
Wood	13	7	31	1.2						4	
Plastic	3.5	0.7	11		8	4.1	6.5	2.9	4.2	54	238
Fiber	3.5	0.4	3.1	14	2.7			14	1.7	2	
Rubber			1.8							1	
Unidentified debris	6.7	12	6.1	11	4.1				0.9	8.9	
<u>Natural Types</u>											
Tar	6.7	31	52	1.2		11.4	3.2	2.9	0.9	15	27
Insects	14	12	62	1.2	2.7	4.1				1	
Charcoal			1.2							2	
Kelp	2.6	5.6	63	1.2				2.9	1.7	29	47
Eel grass	0.9	0.8							0.9		
Surf grass	0.9	1.5	3								
Sea lettuce		0.4					1.6			4	3.7
Pumice	1.7										
Feathers			0.6	2.5	1.4	4.1		2.9			
Eggs		1.1	1.2								
Crab		0.3	1.2								
Mysid		0.8									
Siphonophore	0.9	0.8	0.6								
Copepod	2.6	0.3	2.5						36	1	
Sponge	0.9		1.8								
Nauplius											
Dinoflagellate	1.7										
Barnacle											
part. (?)	2.6		4.9								
Eucarida				2.5				34	4.2		3.7
Diatom						5.5	1.6				
Others ^a					1.4	1.4	3.2		1.7		
Total	417	337	1790	37	78	115	139	80	75	345	903

^aPollen, fish, sea spiders, etc.

Table 28. DESCRIPTION OF PARTICULATES:
3.7 KM N OF HYPERION OUTFALL
(no./100 m² trawled)

Trawl No.	IV-7-71			IX-1-71			
	1	2	4	1	3	5	7
<u>Sewage Types</u>							
Grease and wax	39	7	2	38	23	77	90
Seeds	7	11	3	5.5	4.4	25	69
Misc. tissue	5.6	0.3	0.6		1.3		
Wood	4.3	6.3	0.6				
Plastic		0.3	0.6	1.8	0.6	1.4	
Fiber	0.7	0.9	0.9	2.7		4.1	1.5
Rubber					0.6		
Unidentified debris	0.3	1.6	2.8	0.9			
<u>Natural Types</u>							
Tar	2.3	2.2	0.6	5.5	1.3	4.7	2.9
Insects	11	8.5	11	4.6	1.9	1.4	
Charcoal	1			0.9		0.7	
Kelp	4	1.2		21	1.9	34	
Eel grass	16						
Surf grass		0.9					
Pumice	0.7	0.9	0.9	0.9			
Feathers				1.8	0.6		
Eggs		2.2					
Crab			0.3				
Mysid		0.3	0.6				
Siphonophore		5	0.9				
Copepod	0.7	4.7	2.5	1.8		0.7	
Isopod			0.3				
Hydroid			0.6				
Sponge			0.6				
Larvae		0.3	0.3				
Barnacle							
part. (?)		0.9	0.3				
Others ^a		0.3		2.7	0.6		
Total	93	55	30	88	36	149	163

^aPollen, fish, sea spiders, etc.

Table 29. DESCRIPTION OF PARTICULATES COLLECTED: CONTROL AREA
(no./100 m² trawled)

Trawl No.	IV-8-71				IX-2-71			
	1	2	4	5	1	3	5	7
<u>Sewage Types</u>								
Grease and wax	0.5	0.5	2.8					
Seeds		1.5					0.4	
Misc. tissue		0.5						
Wood		2						
Plastic		0.5			0.5	0.3		
Fiber		2.5	0.9		0.5	0.6		
Unidentified debris	0.5	2.5		0.2	0.3			
<u>Natural Types</u>								
Tar	0.5	3	3.8	1.5			3.9 ^b	0.4
Insects	1	7.5	1.9	9.3	0.3		0.9	1.7
Charcoal					0.3			
Kelp	16	54	4.7	1		1.9		
Eel grass					0.8	0.6		0.4
Surf grass	0.5	3.5						
Sea lettuce			0.9					
Red algae		1	0.9					
Feathers					0.3			
Eggs	1	1.5				0.3	0.4	
Crab		0.5						
Mysid				0.2				
Siphonophore		0.5	0.9	0.2				
Copepod	0.5		2.8		0.3			
Isopod		0.5	0.9				1.3	
Hydroid		0.5						
Sponge			0.9					
Nauplius		0.5						
Larvae			0.9	0.8				
Barnacle		11		0.2				
part. (?)								
Coelenterata					0.8	1.6		0.4
Eucarida					0.3	0.6	1.3	7.0
Others ^a		2.5			1.3	1.0	4.4	
Total	20	96	22	13	5.4	7.0	13	9.9

^aPollen, fish, spiders, etc.

^bIncludes one piece 35 x 15 x 2 mm in size.

APPENDIX B

ANALYTICAL METHODS

The ocean surface and bulk samples, and the 24-hour composited bulk effluent samples, were processed as indicated in the scheme of analyses shown in Figure 31. Details of sample collection were presented in the appropriate sections of the report. The processing of samples collected by the various samplers and the methods of analyses are presented below.

CLOTH SCREEN SAMPLES

The hexane extractables were obtained from the glass cloth screens by removing the cloths from their containers and allowing them to air dry in a hood. The cloths were then extracted for one hour in a standard soxhlet apparatus and concentrated to 5 ml for transfer. The residue was dried under nitrogen at 40°C and weighed for hexane extractables. This material was retained for subsequent fatty acid and chlorinated hydrocarbon analyses.

The coliform organisms, surface plankton, and micro-particulates were washed from the nylon netting screens and filtered. Sterile buffer solution (150 ml) was used to wash the coliforms from the net screens and appropriate aliquots were then filtered immediately through membrane filters and incubated for later counting in the laboratory in accord with Standard Methods [5]. For the surface plankton and micro-particulate determinations, however, the wash water was filtered sea water and the sampler washing procedure was repeated twice with the filtered material being counted and identified directly on the membrane filter.

FLOATING PARTICULATES

The floating particulate samples were washed with distilled water, dried at 35°C, and weighed. For the first two surveys the particulates were counted and identified directly under a dissecting microscope. The particulates were then extracted with hexane for one hour in an alumina thimble in a standard soxhlet apparatus. The residual was then evaporated and weighed for hexane extractables.

SAMPLES

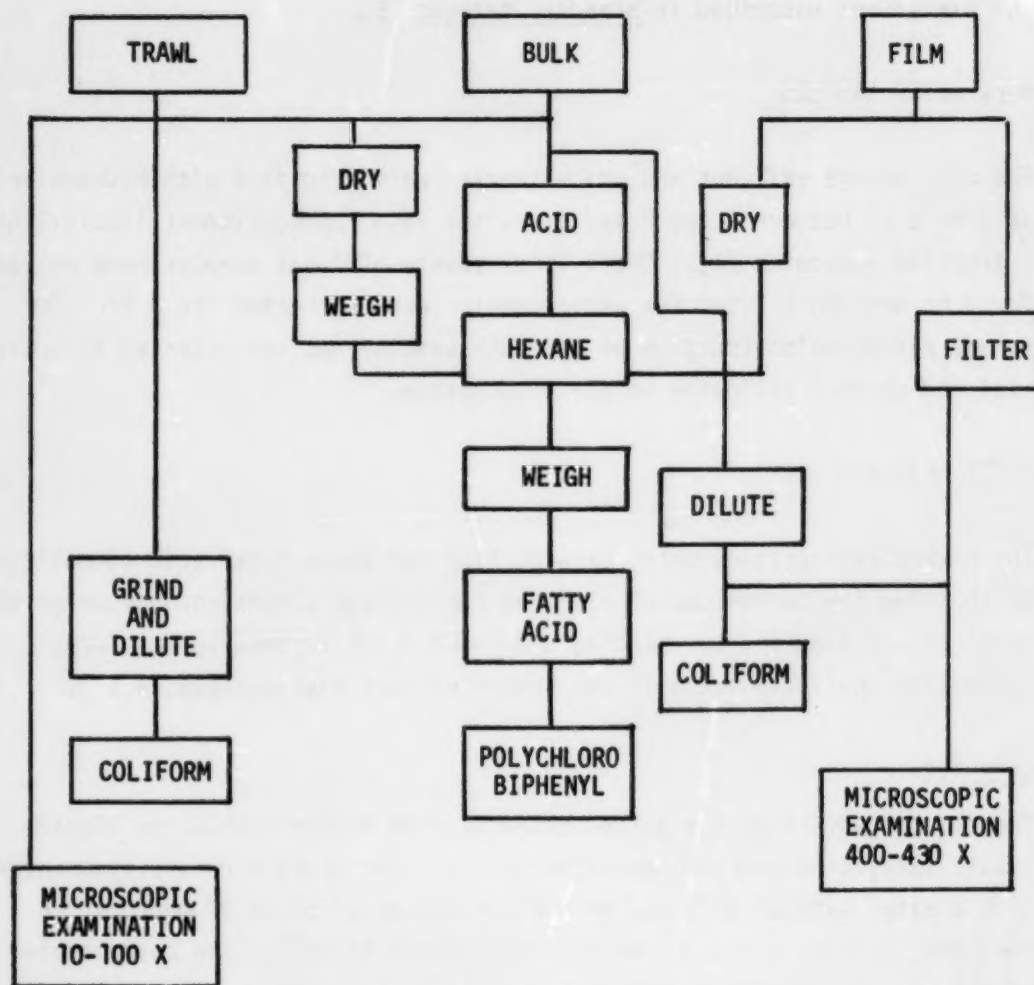


Figure 31. Analytical Approach to Characterizing Flotage and Bulk Samples

Particulate samples selected for coliform organism analysis were processed as soon as possible at dockside. The particulates were homogenized in a sterile buffer solution of known volume, and appropriate aliquots of the homogenized mixture were filtered through membrane filters in accord with the procedures described in Standard Methods [5].

BULK WATER SAMPLES

The bulk sewage effluent and ocean samples were acidified with hydrochloric acid to a pH between 1 and 2 and extracted in a Pearson-Thomas liquid-liquid extraction apparatus [8]. The 1 liter sewage effluent samples were extracted for 3 hr and the 4 liter sea water samples were extracted for 9 hr. The hexane extractables fraction of the bulk samples was concentrated in a tared vial and weighed following hexane evaporation.

FATTY ACID ANALYSIS

The hexane extractables were characterized for their fatty acid composition by applying the techniques of electron capture gas chromatography using the novel esters prepared by reacting α -bromo-2,3,4,5,6-pentafluorotoluene (BFT) with the fatty acids in the hexane extract residues [15,16,17].

Weighing

The flasks containing the hexane extracts from either soxhlet or liquid-liquid extraction were concentrated to 1 or 2 ml using a rotary evaporator with a water bath at 40°C and an applied vacuum of 50 mm of mercury. A one gram, 1.3 ml, glass, tared vial was heated to 40°C. The concentrated sample was transferred to the vial quantitatively with hexane using a jet of high purity nitrogen gas to assist in the evaporation of the solvent in the vial. After cooling in a dessicator the vial was weighed to $\pm 10 \mu\text{g}$.

Reaction

After weighing, the sample was quantitatively transferred back to its original flask using 10 ml hexane and dried on the rotary evaporator. To

the flask were then added approximately 12 mg of K_2CO_3 (powdered and dried at $103^\circ C$) followed by 10 ml of acetone (Nano Grade[®]) and 0.1 ml of 5 percent α -bromo-2,3,4,5,6-pentafluorotoluene (BFT) dissolved in absolute ethanol. The flask was then connected to a condenser, the ground glass fitting wetted with acetone, and the open end of the condenser covered with aluminum foil. The mixture was refluxed for one hour and cooled in a $20^\circ C$ water bath for approximately 10 minutes before disconnecting the flask from the condenser. (Note: Any water present in the sample grossly inhibits this reaction.) The acetone was removed on the rotary evaporator as before and the reacted sample was then quantitatively transferred with hexane to a 10 ml volumetric flask.

Chromatography

One micro-liter samples were then injected into two gas chromatographs. Model 1200 Varian Aerographs were employed in the study, both equipped with concentric tube electron capture detectors (^3H , 250 mCi). Two different analytical GLC columns were used, one in each chromatograph. The columns were 1/8 inch by 6 ft Pyrex[®] glass packed with 2.5 percent QF-1 on Varaport 30 (80/100 mesh) and 5 percent QF-1 plus 3 percent DC 200 on Chromosorb Q (80/100 mesh). The use of both columns permitted resolution of the fatty acids into saturated and unsaturated components and provided presumptive evidence for identification of compounds by comparison of retention times with standards. The carrier gas (purified N_2) was maintained at approximately 50 ml min^{-1} ; and the injector, column, and foil temperatures were $230^\circ C$, $190^\circ C$, and $200^\circ C$, respectively, in both chromatographs.

CHLORINATED HYDROCARBON ANALYSES

The cleanup of hexane extracts for chlorinated hydrocarbon analysis was conducted with liquid chromatography in Florisil as described by Reynolds [18] and Veigh [19]. The media was purchased from Varian Aerograph in the purified and activated (at $650^\circ C$) form and kept at $130^\circ C$ prior to use. The column was 25 mm o.d. with a narrow discharge neck at the bottom fitted with hexane extracted glass wool and a 250 ml solvent reservoir at the top.

Twenty grams of Florisil were added to the column topped with ten grams of anhydrous sodium sulfate for removal of possible trace water present in the extract. The column was washed with 70 ml hexane which was discarded, followed by 20 ml hexane used as a blank. The extract was then placed on the column and eluted with 200 ml hexane to recover DDE and PCB primarily. A second fraction was then collected by eluting with 20 ml of 20 percent ethyl ether in hexane to obtain DDT, dieldrin, and other more polar chlorinated hydrocarbons. If the hexane extract had been reacted with BFT, these esters were also eluted in the second fraction. Control showed that PCB's were not affected during the BFT reaction.

The eluants were then concentrated to volumes of 1 ml or 10 ml, and one micro-liter volumes were injected into the same columns used for the fatty acid analysis.

STANDARDS

Fatty acids of 99+ percent purity were purchased from Applied Science Laboratories, Inc. These were weighed and reacted with α -bromo-2,3,4,5,6-pentafluorotoluene, Puriss Grade[®] (molecular weight 260.99) purchased from Aldrich Chemical Company, Inc. The completion of the reaction and recovery of the ester was confirmed by comparison with known amounts of similar esters supplied by Dr. Kawahara of the Analytical Quality Control Laboratory, EPA in Cincinnati, Ohio.

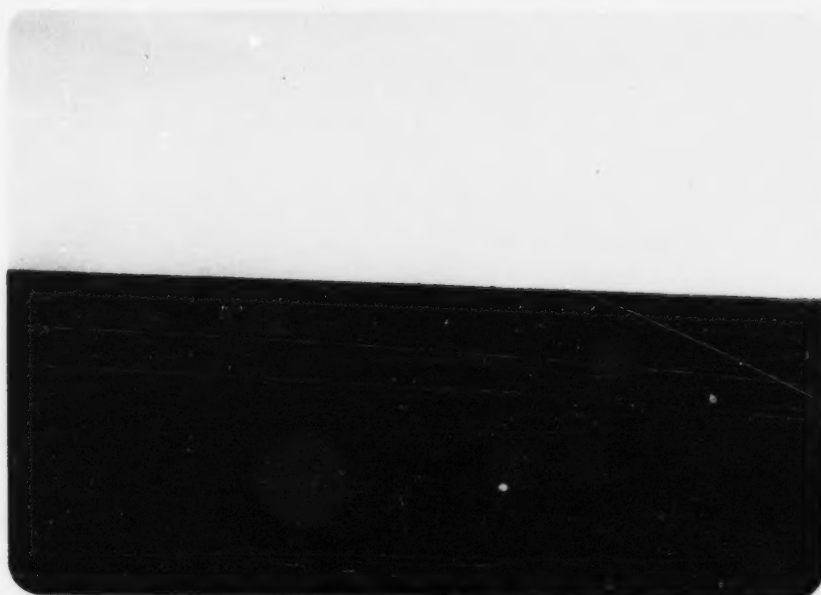
PCB standards for Aroclor 1242, 1248, 1254, and 1260 were obtained from Dr. Joseph Blazeovich of the EPA Laboratory in Corvallis, Oregon. Chlorinated insecticide standards were purchased from Varian Aerograph.

CONTROLS

All hexane purchased was of Nano Grade[®] quality and redistilled in glass before use. Potassium hydroxide pellets were placed in the distilling flask. All glassware was cleaned with a hot dichromate in sulfuric acid cleaning

solution, rinsed with distilled water, baked out at 103°C, and purged with nitrogen gas while still hot. Blanks were run frequently on reagents and glassware for contamination monitoring.

The fiberglass cloth samplers were washed in distilled water and then air dried in a hood. The cloths were then soaked in a 60°C dichromate and acid cleaning solution (heated initially only) for twenty four hours after which they were removed, washed with tap water, rinsed with distilled water and then air dried as before. The cloths were then placed in a 4 liter bottle of hexane with a few pellets of KOH in the bottom, a reflux condenser fitted to the bottle's tapered glass joint and the hexane refluxed on a hot plate for 4 hours. The cloths were then extracted in soxhlet extractors, 2 to a soxhlet for 4 hours with hexane plus a few pellets of potassium hydroxide. Fresh hexane, distilled in glass from pesticide quality hexane was then used to extract the cloths for 2 more hours (no potassium hydroxide present). The extracts from 6 soxhlets were then combined, dried, and weighed to determine the cleanliness of the extracted cloths. The hexane residue was then reacted with BFT and the fatty acids present determined by GLC to determine cloth background levels.



Hyperion, September 1, 1971



JWPCP, July 11, 1973

Figure 15. Photographs of Sea Slicks Over Hyperion and JWPCP Outfalls

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Figure.18. Rise of Large Particulates in the Vicinity of the L Diffuser of the JWPCP Outfalls: July, 1973

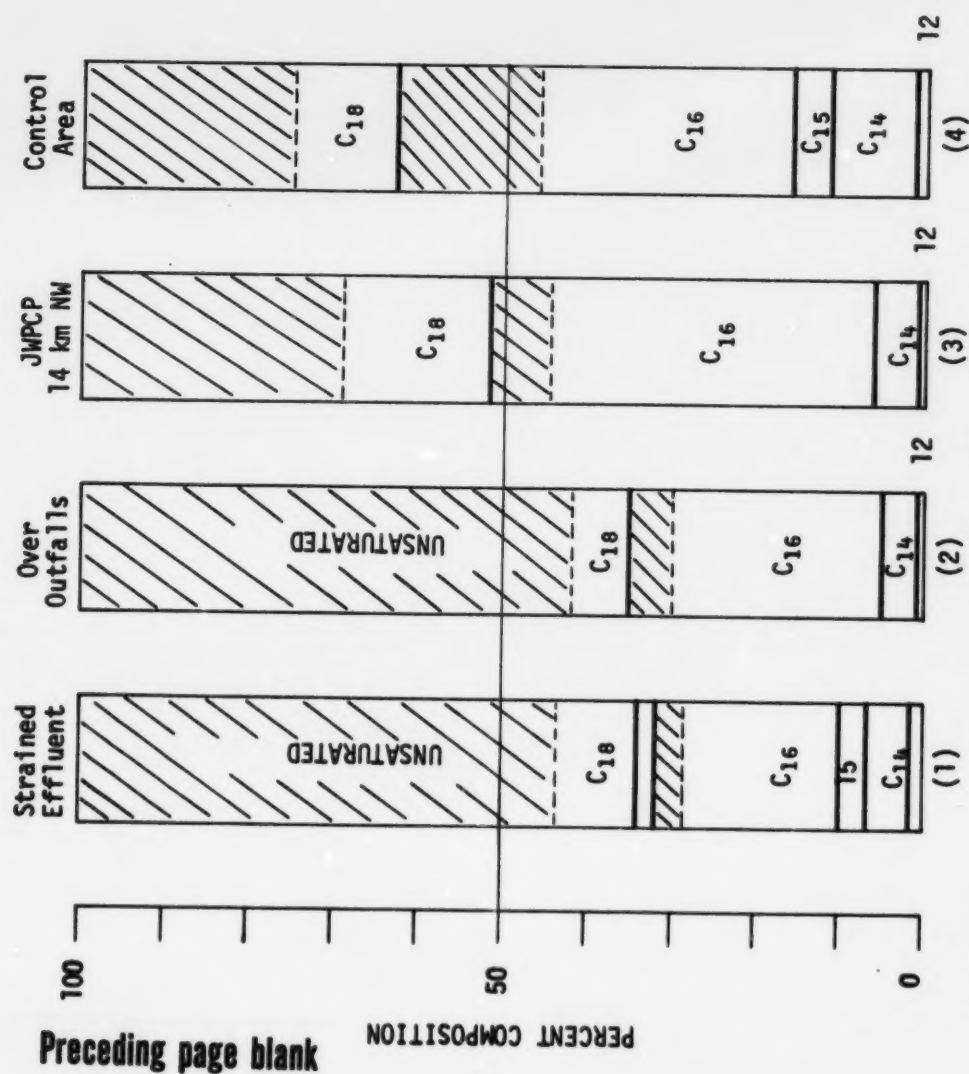


Figure 19. Fatty Acid Composition of Large Particulates: July, 1973.